Why ask for the moon
when we have the stars?

AS

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Section 13

Natural History Collections

Collections d'histoire naturelle

ASPECTS OF THE BIOLOGY OF THE GUERNSEY CARPET BEETLE, *ANTHRENUS SARNICUS* MROCZK., AND CONTROL OF DERMESTID BEETLE PESTS IN MUSEUMS

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SUMMARY

Following serious damage to zoological collections at the British Museum (Natural History) by a carpet beetle, *Anthrenus sarnicus* Mroczk., a research project was initiated to study its' biology and control in museums. This 'newly' discovered insect has become a widespread domestic pest in the London area and poses a new threat to museums. Sticky-traps have been used to successfully monitor pest populations in museum buildings, and data obtained has highlighted the extent of the pest problem. Cultural control methods such as removal of birds' nests from roof spaces and ventilation ducts, and fluff and debris from working areas, are important in eliminating potential foci of infestations. Treatment of new and returning specimens entering museums by fumigation, heat or freezing techniques are important in preventing introduced pests becoming established in buildings. Many current chemical control methods are inadequate and lack scientifically based efficacy data. Research is currently in progress to determine the effectiveness of a range of low mammalian toxicity insecticides for use in museums.

INTRODUCTION

Infestations of a 'new' museum pest, the Guernsey carpet beetle, *Anthrenus sarnicus* Mroczk., (Coleoptera: Dermestidae), were discovered in collections of the British Museum (Natural History), (BMNH), in 1973, and within five years it had become the most serious pest damaging insect and stuffed animal collections in the museum. Prior to its' discovery, the museum had suffered only small, sporadic infestations of the native Dermestid beetles. Th early 1980's saw an alarming population explosion of this beetle, and it rapidly became apparent that current pest control methods were ineffective at preventing damage to specimens. Museum staff had little knowledge to fall back on, there was no published data on the pest's biology, and only scant information regarding the use and safety of insecticides in museums. In 1981 a research project was initiated by the Entomology Department of the BMNH in collaboration with Imperial College, University of London, to investigate the biology of *A.sarnicus* and more generally, the control of Dermestid beetles in museums.

A.sarnicus was first recorded in Guernsey, Channel Islands in 1961 from a domestic infestation, where larvae had caused considerable damage to clothing in cupboards (Edwards, 1969). The next record of this new species was from London in 1963, subsequently its' distribution spread rapidly, now being fairly widespread in SW. and W. postal districts of London. Further domestic infestations have been recorded in Wiltshire (Woodroffe, 1967), Amsterdam, Netherlands (Anon, 1975), and the first museum infestation outside London was recorded from Liverpool in 1982 (unpublished), where larvae were damaging butterfly collections.

The larvae like those of other *Anthrenus* species will feed on any dry matter of animal origin. In domestic infestations larvae have been found damaging clothing, carpets, feeding on fluff and food debris accumulated in cracks in floorboards, and thriving on a dead pigeon behind a panel covering a disused fireplace (Woodroffe, 1967). Museums provide a wealth of potential food sources for such pests, insect collections, stuffed animals, human artefacts, and leather book-bindings to name but a few; many are irreplaceable and all susceptible to damage unless adequate pest control techniques are employed.

Apart from a thorough investigation of the beetle's biology, which is beyond the scope of this paper, research has been directed at monitoring pest populations and determining the efficacy of pesticides in eliminating damaging pests, but at the same time causing minimal health hazards to people working with the collections, or damage to the collections themselves. Experiments have been directed at the control of pest damage to insect collections, but it is hoped that the final results will be of use to other areas of museum pest control.

MONITORING PEST POPULATIONS

Upon commencing this study it was decided that an important facet of a control programme was to monitor pest populations in the museum buildings. At the BMNH successful monitoring has been achieved firstly by making staff aware of the pest problem through newsletters and bulletins requesting that they look out for and collect potential pest insects they find in the collections and their working area, and secondly by the use of sticky-traps. Most stored products beetles are attracted to light at some period during their adult life, indeed often the first indication of an infestation of *A.sarnicus* is the congregation of adults at windows and other well illuminiated areas. By applying plastic tape along window ledges and coating this with a liberal layer of a highly sticky banding gum, 'Stick-Em' (J.T. Eaton & Co., Inc.), this light positive behaviour has been used to intercept flying adults. Unilluminated areas such as store-rooms have been monitored by suspending an electric light bulb over a clear plastic cylinder coated with banding gum, adults are attracted to the light, which incidently should be the only source of illumination in the room, and are intercepted by the sticky-trap. Sticky-bands remain effective for eight to twelve months before they need to be replaced because of diminished tackiness through accumulations of dust and debris.

Traps are checked weekly and all trapped insects, along with those found by staff vigilence are sent to a central co-ordinator in the Entomology Department for identification and recording. Within a few weeks of starting the programme the scale of the pest problem soon became apparent. Window trapping identified a number of pest insects which had not previously been recorded in the museum, and also indicated that different pest problems were to be encountered in different areas of the museum (Table 1). *A.sarnicus* was by far the most numerous pest caught in the traps and poses the greatest threat to zoological collections.

Trapping data has also revealed adult emergence patterns of these pest insects throughout the year. For example, in 1983 (Fig. 1), *A.sarnicus* adults appeared in early June, reached their peak abundance in July and had virtually disappeared by mid-September. Such information is important in determining the timing of control measures, use of a suitable insecticide in collection cabinets just prior to the period of activity of gravid females could be sufficient to prevent oviposition and immigration of young larvae into the collections. If trap data is collected over a number of years, the effectiveness of newly implemented control strategies can be determined by fluctuations in pest populations.

	ENTOMOLOGY BUILDING	GENERAL HERBARIUM
Guernsey carpet beetle, *Anthrenus sarnicus*	531	846
Lesser grain borer, *Rhyzopertha dominica*	-	503
Biscuit beetle, *Stegobium paniceum*	36	41
Carpet beetle, *Reesa vespulae*	34	1
Carpet beetle, *Attagenus smirnovi*	26	-
Dark carpet beetle, *Anthrenus fuscus*	6	-
Case bearing clothes moth, *Tinaea pellionella*	-	4
Varied carpet beetle, *Anthrenus verbasci*	1	-
Carpet beetle, *Anthrenus coloratus*	1	-

TABLE 1. Total numbers of stored products pest caught at window traps in two departments of the BMNH in 1983.

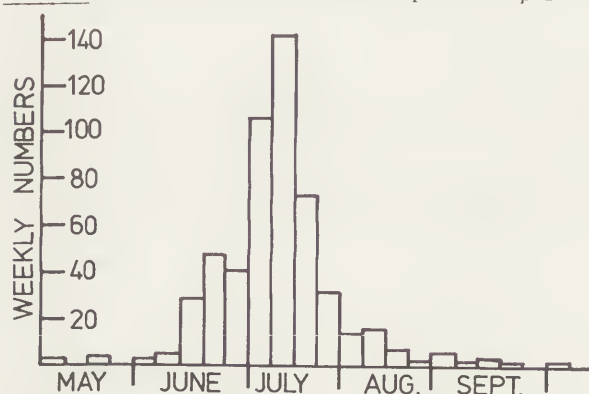
FIGURE 1. 1983 weekly window captures of *A.sarnicus* in the BMNH Entomology Building.

PREVENTION & CONTROL

It is more important to prevent attack by museum pests than to control them once they are found. To this end 'cultural control' methods can go a long way to reducing the likelihood of infestation of collections. The natural habitats of most Dermestid beetles are the nests of birds, mammals, and insects, here the larvae feed on dried carcasses, dead insects, fur and feathers. Man's use and storage of dried animal products has provided addtional habitats for these natural scavengers. Birds' nests in roof spaces and eaves often prove to be the source of infestations in buildings, if these foci are not eliminated then there is always the likelihood of diffuse re-infestation from larvae migrating from roof spaces and ducts, and from adult beetles flying in through open windows etc. At the BMNH nests and guano of the city pigeon in ventilation grilles and heating towers were found to be harbouring populations of Dermestids, these sources have mostly been eliminated by removal of birds' nests and proofing of the building to prevent further nest building. In addition, accumulations of fluff, dust and debris between cracks in flooring and under cabinet plinths etc., provide ideal breeding sites inside buildings.

Ideally the entry of pests into collection material could be barred through the use of effectively air-tight container systems. It has been observed at the BMNH that metal carcassed cabinets with rubber door seals are far less prone to pest attack, compared with those with wooden carcasses, despite the fact that both have wooden drawers inside. Unfortunately the change over to new cabinet systems in most museums is cost prohibitive and many fine collections are still housed in the old cabinets and boxes in which they were inherited from private collectors.

Four of the nine pest insects listed in Table 1 are not native to the British Isles, and have probably been introduced to the museum through the incorporation into the collections of new and returning specimens without prior treatment to ensure they are pest free. Large specimens should be fumigated with methyl bromide using proper fumigation apparatus, smaller specimens can be successfully 'sterilised' using temperature treatments. The Entomology Department installed a large laboratory oven for this purpose.

Boxed specimens are heated to 50° C., for at least 24 hours, this has been found to be effective in killing all developmental stages of pests encountered and no adverse effects have been observed to specimens or boxes, including plastic specimen drawers. The use of heat in combination with relatively high humidity has been used at other institutions to control pest infestations in botanical collections.

Freezing is another technique which is effective in eliminating established infestations, Crisafulli (1980) quotes a number of institutions where deep-freezing at temperatures of -18 to 40° C., for two days to one week has been effective in controlling herbarium pests. Deep-freezing of insect cabinet drawers at -20° C., for 24 hours is effective in killing all stages of *Anthrenus*. After treatment boxes should be left to warm-up to room temperature before opening, otherwise condensation can be a problem.

Napthalene and paradichlorobenzene (PDB), are the two chemicals most frequently used for the prophylactic treatment of specimen drawers and boxes in museums. Both have only limited insecticidal efficacy and are used because of tradition, ease of handling and supposed safety rather than any scientific knowledge of their effectiveness. Indeed, a survey of American museums by Bell and Stanley (1981), showed that 68, 40, and 27 percent of respondents used PDB, Vapona and napthalene respectively to control pests, and 40 percent of respondents gave tradition as the reason for using these pesticides. 34 percent of respondents used pesticides such as PDB, napthalene, Vapona and pyrethrins because they considered them to be safe.

PDB is more toxic to insects than napthalene, which is considered a repellent rather than an insecticide, but volatilises quicker and therefore does not last as long. For either chemical to be effective an excess of crystals must be present, neither has any repellent effect at sub-lethal concentrations. PDB softens and 'melts' certain plastics and can affect colours of specimens.

Dichlorvos slow-release units (e.g. Vapona), have been used successfully in museums for a number of years. Scudamore et al (1980), found that such units used at between one and six times the recommended rate for normal domestic or industrial use in display cases and cabinets was sufficient to protect specimens from attack by insect pests for six months or more. Maximum air concentrations of dichlorvos vapour both inside and outside cabinets did not exceed specified safety levels. According to Ryckman (1969), Vapona Insecticide Pest Strips used in wooden insect boxes were effective in preventing pest attack for up to two years. Despite its obvious effectiveness many museums are not prepared to use dichlorvos because of fears regarding health hazards and because of its corrosive properties towards metals and staining of specimens.

PDB, Napthalene and dichlorvos, are termed 'space fumigants' because when in solid or liquid formulations in an enclosed space, the active ingredient volatilises over a period of time producing a toxic fumigant vapour. Insecticides toxic to insects in the vapour phase are

useful in museums as it is usually not feasible to apply contact pesticides directly to specimens without causing damage, and there is also the chance that the pest insect will not come into direct contact with the chemical anyway. Fumigants on the other hand will diffuse into the specimens to be protected, killing the pests either by the direct fumigant action of the vapour, or through contact or ingestion of insecticide absorbed onto the specimens. The property of volatilisation is partly dependant upon the vapour pressure of the chemical, insecticides considered as space fumigants have relatively high vapour pressures ($\geqslant 10^{-2}$ torr at 20° C.), but many chemicals used as contact insecticides have a sufficiently high vapour pressure (10^{-4}-10^{-6} torr at 20° C.), to be effective in killing pests in the vapour phase if confined in an enclosed space. Because these chemicals have lower vapour pressures than traditional space fumigants, diffusion of the insecticide into the vapour phase occurs at a much slower rate for a given temperature, thereby increasing the length of time that a treatment remains effective (Fig. 2), and reducing the concentration of insecticide vapour in the atmosphere of the building.
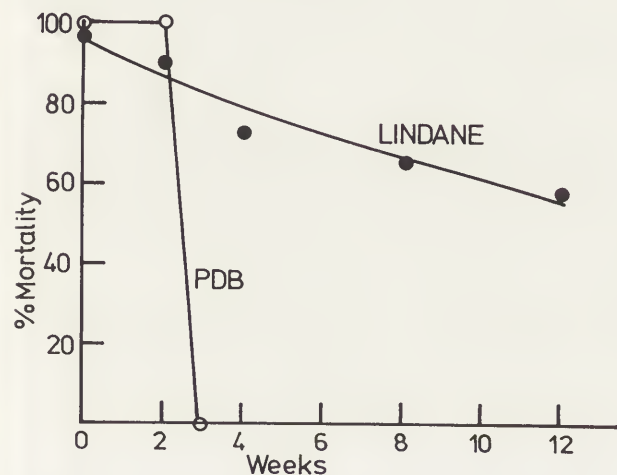

FIGURE 2. Vapour phase toxicities to early instar *Anthrenus* larvae (24hr. exposure at 25° C.), of PDB (v.p.6.9x10^{-1}torr at 20° C), and Lindane (v.p.9.4x10^{-6} torr at 20° C.), applied to wooden boxes at rates of 2000gm/m^3 and 0.75gm/m^3 respectively.

A range of insecticides which have been cleared in the UK for use against storage, domestic and hygiene pests, are currently under investigation for museum use. The effectiveness of these insecticides is being considered with regard to: minimum effective concentrations and the efficacy of fumigant and contact activity against developmental stages of Dermestid pests; persistance of insecticide deposits in museum boxes and their effect on substrates to which they are applied, and mammalian toxicity.

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NATURAL SCIENCE COLLECTIONS AS A GLOBAL DATA BANK

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SUMMARY

Natural science specimens are ideal for eva-
luating the past and present condition of
the earth. The maintenance of such collec-
tions is expensive, for the objects are
often fragile and rare. Furthermore, these
collections, by their very nature, must grow
with time and thus require increasing space
to house them. Criteria for accessioning
and deaccessioning specimens, rate of
collections growth and storage methods are
discussed. The Smithsonian's new Museum
Support Center (MSC) is presented as a
current solution to the problem of efficient
storage and maintenance of collections.
Directors of major natural history museums
are responsible for maintaining and judi-
ciously expanding their collections, which
serve as a data bank to monitor the state of
the globe.

The collections of natural history museums
function as a chronicle of the world's
history from its very beginning, through the
origin of life, to its present condition.
These collections are the equivalent of an
enormous book of knowledge, but not every
page or chapter is equally readable. The
type may be bold and clear or so indistinct
as to be illegible. However, with each new
technical advance, such as that of potassium
argon dating, pages and even whole chapters
become suddenly clear. With time our chro-
nicle of the earth's history becomes ever
more complete, but always dependent on the
collections of natural science still waiting
to be "read" by future generations.

Although keeping books in a library is
expensive and time consuming, it is even
more costly to maintain collections in a
museum. To retain their value, museum spe-
cimens have not only to be preserved as
close to their original condition as
possible, but also they must be available
for study. At first glance this seems a
simple requirement, but museum professionals
know that constant vigilance is needed to
keep specimens from gradual deterioration
and loss. In addition to data on the
collections, museums keep records of events
that do not primarily involve objects, such
as photographs or eye witness accounts of
volcanic eruptions or large cultural
gatherings. Today there are probably only a
few dozen large natural history museums that
meet all the necessary criteria of per-
manence and care to qualify as global data
banks.

Now, more than ever in recorded history,
mankind is faced with enormous losses of
species and degradation of the environment
and native cultures. Museums must respond
to these global changes through collecting
and documenting biota, cultural artifacts,
fossils and geologic specimens before they
and the information they contain are
severely altered or destroyed.

Problems in maintenance and conservation of
specimens are varied and often difficult to
resolve. Feathers and furs, for example,
are harder to store than are specimens of
minerals and many fossils. Insects can
attack the former and exposure to light,
particularly in the ultra-violet, can cause
their disintegration. As our knowledge of
the chemical characteristics of specimens
improves, so do our methods for their pre-
servation. For example, collections of
fish, amphibia, and marine invertebrates
used to be kept in soapstone tanks of for-
malin. Veteran museum workers can recall
this foul smelling chemical whose stench was
characteristic of museum storage rooms.
Today these specimens are kept in tightly
sealed jars of alcohol, a better smelling
chemical but one which evaporates so rapidly
when exposed to air, that every jar has to
be regularly checked for air leaks.

Today computers allow the maintenance of
incredibly detailed records of specimens and
their storage locations. However, com-
puterized records require that every signi-
ficant piece of information (catalogue
number, identification, location in the
museum, condition, etc.) of each specimen
must be entered into a terminal. The
Smithsonian began using computers to record
data on some of its natural history collec-
tions more than a decade ago. Today, the
Institution is finishing a complete com-
puterized inventory of all its collections.
When done, we will know what we do have, but
not necessarily what our records show that
we ought to have. A full reconciliation
requires comparing current inventory lists
against old accession records, many of which
are incomplete. Of the 100 million or so
natural history specimens inventoried, we
have been surprised at finding many objects
we did not know we owned. We failed to find
only very few that our records indicated
should be on hand. It is unlikely we will
ever perfectly reconcile the collection
records, but at least we will know
everything in the collections in 1983. This
five-year inventory required about 400
people working full-time for the Natural
History Museum alone and cost roughly 10
million dollars. In addition, the museum
will require some 500 hundred thousand
dollars each year to keep its records
current. This money will be well-spent.
With good computerized records, it is rela-
tively easy to incorporate data on new
acquisitions into the inventory data file.

Once accessioned and safely stored, a speci-
men may remain untouched and unstudied for
decades. Despite its seemingly static con-
dition, each such specimen is, nonetheless,
a dynamic source of information--a page
waiting to be read. Also, through refine-
ments in dating techniques, new knowledge
can be extracted from previously studied
artifacts. Archeometry has become an impor-
tant diagnostic tool in evaluating human
artifacts. This discipline integrates
archeological, anthropological, and art
historical data of an artifact to discover
when, how and by whom it might have been
made. Techniques range from dendrochronolo-
gical dating (using variation in tree ring
width) of large wooden statues to geochemi-
cal dating of fossils, by measuring the

decay of their radioactive potassium into argon. In biological investigations the more precisely we can determine the age of a fossil, the more obvious becomes its place in the evolutionary hierarchy. In like manner, careful dating by archeometry of artifacts is invaluable in understanding the sequences of cultural development.

In fact, the very existence of natural history collections let us answer questions not only about the past, but also about present ecological conditions. Using museum collections of eggs, for example, scientists tracked the consequences of using DDT throughout the world, by comparing egg shell thickness in certain susceptible species before and after the introduction of this pesticide. Likewise museum osteological collections of Antarctic birds and mammals can tell us how long it took strontium-90 to reach that remote continent after the first nuclear explosions. Thus, physically static museum specimens can be "read" by an investigator in new and unexpected ways and continually increase the capacity of museum collections to be tapped as a global data bank.

A good data bank continually expands its base. The base of a natural history museum is its collections. The greatest challenge facing such museums today is to manage the inevitable demand for more space. Museums, by their very nature must increase their collections merely to stay current. However, growth is not indiscriminate and before accepting any specimen, a museum is responsible for documenting provenance to insure that the object can be legally and ethically acquired. Furthermore, sufficient physical, personnel and monetary resources should be available to care for it.

Existing natural history collections are qualitatively enhanced by culling and reorganizing when they are processed, catalogued, and researched. Many collections are refused for poor quality. New collections are normally culled before being accessioned. New field collections are culled initially before shipment. Subsequent culling of these highly-documented research collections will be minimal, generally eliminating only damaged specimens. Figure 1 demonstrates in graphic

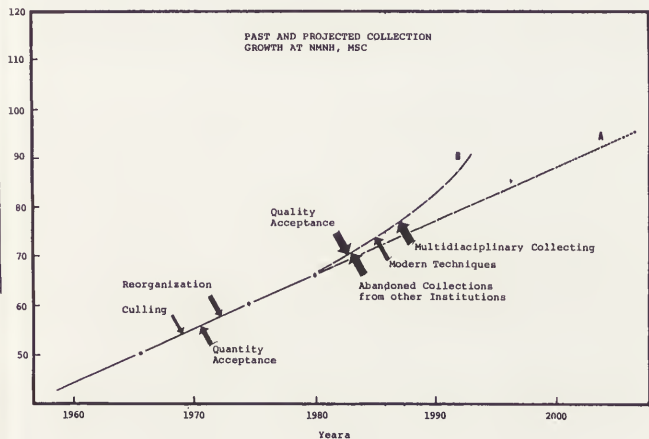PAST AND PROJECTED COLLECTION GROWTH AT NMNH, MSC

Figure 1: Projected collection growth at Natural History Museum and MSC through year 2000 based on: growth rate of 1.87% (actual rate of increase 1966 to 1976); and expected growth rate of 2.35%. Upward arrows show pressures increasing growth rates; downward arrows show pressures reducing growth rates. Thickness of arrows indicate importance of factors. (Terry Erwin, Smithsonian Inst.)

form the forces that tend to change the rate at which collections grow. Culling, reorganization and quality acceptance practices tend to reduce growth, but acceptance of collections abandoned by other institutions, modern collecting techniques, and multi-disciplinary studies increase it.

Today's new acquisition will be tomorrow's relic against which we will compare past and present global conditions. As collections cannot expand at the current rate indefinitely, new ways must be found to refine storage and maintenance techniques. We must also learn to extract more and more information from ever diminishing numbers of new specimens as the constraints of storage space for them become greater.

One approach to meeting the storage problem for the next century is the Smithsonian's new Museum Support Center (MSC). Planning for the MSC started in 1968 when it became evident that the Smithsonian's old Natural History Museum on the Mall (completed in 1914) had long since reached its capacity to house its collections, despite two large wings added in the early 1960's. Storage cases lined every hall and such space demanding specimens, as whale skeletons, were temporarily kept in an abandoned torpedo factory in nearby Virginia. The insect collection lay in rented quarters, and every time such fragile objects were moved the risk of permanent damage to them increased. Furthermore, the Institution's priority for the use of space in such a large public building as the Natural History Museum was for exhibition and education programs rather than for the maintenance of collections that might be studied infrequently.

After a long search a suitable 100 acre site was found in a nearby Washington suburb, about a 20 minute drive from the Museum. Plans were begun for the facility on about 5 acres. In 1978 construction was authorized by the U.S. Congress. All the while curators and collection managers sought to determine the requirements of an ideal facility. The challenge was to have a structure able to handle the Institution's expanding natural history collections into the XXI century. As is often the case, conflicting pressures were rampant. For example, too long a delay in completing the MSC could result in further risk of damaging collections in a move to another temporary storage site; yet it would be impractical to move the collections until the current inventory at the Natural History Museum was complete. Fortunately all the major conditions were met and the move to the MSC started from the Museum of Natural History in late summer 1983.

The MSC is comprised of three areas: the four large pods (each 240 feet (72m) long by 150 feet (45m) wide), a connecting hallway called "The Street," and a two-floor laboratory wing (see Illustration 1 and Figure 2). The pods are windowless and air is circulated through an elaborate filtering system to control the damaging effects that light, dust and pest infestation can have on the collections. One of the most important criteria in maintaining collections for long periods of time is to provide stable, non-fluctuating environmental conditions. The MSC was built to maintain optimal conditions, in both the pods and the laboratory wing, of 70 degrees Fahrenheit (21C), plus or minus 2 degrees Fahrenheit, and 50 percent relative humidity, plus or minus 2 percent.
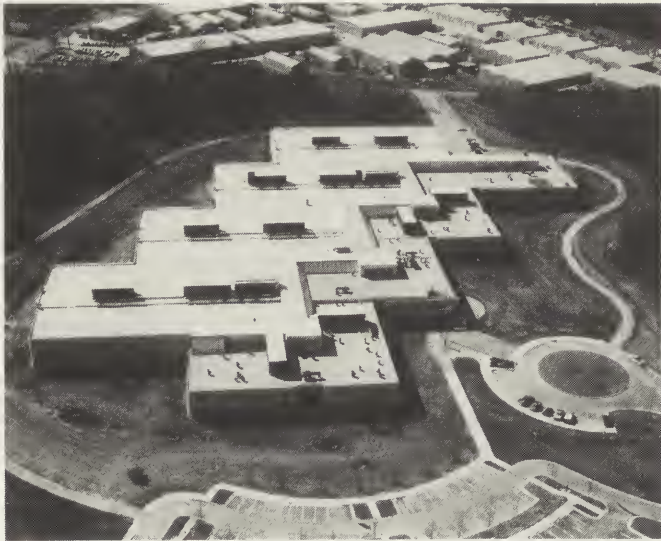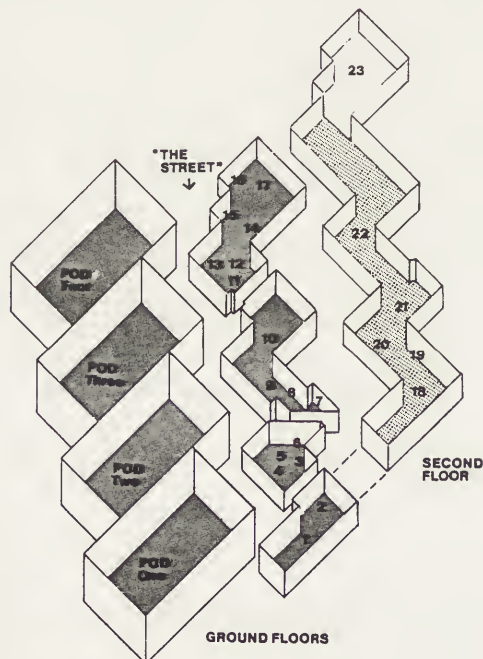
Illustration 1: The zigzag design of the MSC creates maximum adjacency between the four storage pods and the separate, two-story laboratory wing. It also makes the building easily expandable. (Photo Jeff Tinsley)

Figure 2: Drawing by Polly Sexton, The Smithsonian TORCH.

Legend for Museum Support Center Floor Plan

1 Anthropology	12 Building manager
2 Botany	13 Protection services
3 Mineral Science	14 Shipping, receiving
4 Paleobiology	fumigation
5 Entomology	15 Loading dock
6 Administration	16 Plant services
7 Food service	17 Energy plant
8 Vertebrate Zoology	18 Anthropology
9 Invertebrate Zoology	19 American History
10 Oceanographic Sorting	20 Photography lab
Center	21 Library
11 ADP/Registrar	22 Conservation Analytical
	Lab

"The Street" connects the storage pods with the laboratory wing. Scientists and collection management personnel work on collections in laboratories adjacent to the pods avoiding the need to transport specimens back to the museum downtown. In addition, the MSC contains the Conservation Analytical Laboratory, a facility with a staff of 50 which develops and improves techniques to preserve and restore objects.

Within the pods the collections are stored in the most efficient, cost effective way that the planners could design. Modular units were designed in which tray, drawer and shelf sizes were correlated with the dimensions of a significant majority of the items to be stored. After many measurements, four common drawer/shelf modules were determined to be adequate to store almost all objects. These four different sized units are fabricated in turn so that they fit, in various combinations, into a standard steel framework (see Illustration 2). The framework is a free standing, self-supporting unit, three stories (24 feet/7.2m) high and has heating, ventilating, air conditioning, electrical and fire safety systems on all three levels.
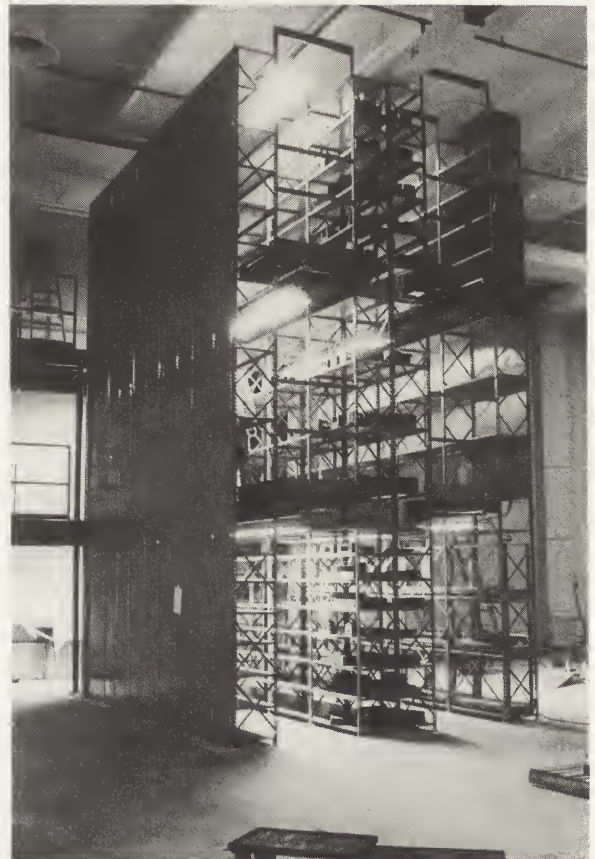
Illustration 2: Collection storage shelving for specimens preserved in alcohol and stored in bottles or tanks. Note mechanical ductwork, lighting and sprinkler systems at all three levels. (Photo Jeffrey Ploskonka)

The framework, in turn, is assembled in the four pods and the design is flexible enough to allow the modules to be open for storage of such relatively imperishable objects as elephant skulls and mineral specimens or to be enclosed by light, dust, and insect tight panels to store fragile objects. The storage frameworks are carefully located to allow for expansion within each discipline as its collection grows.

Despite this seemingly enormous space for Smithsonian collections, the staff projected that the natural history collections may fill all available space by the turn of the century if the current rate of acquisition continues. Fortunately the facility was designed so that each pod can be lengthened and at least one additional pod can be easily added in the future.

Future museum directors face the same dilemma as their predecessors: which collections to accept and which to reject from

among myriad offerings. Eventually even
large well-supported museums may have to
consider following a trend already evident
among small natural history museums, i.e.,
toward con centrating in specific areas such
as paleontology, vertebrate zoology or
anthropology. Ideally collections might be
gradually shifted until each of the world's
museums achieves a disciplinary con-
centration. However, pressure for such con-
centration will have to be considerably
greater than it is now for any such an
exchange to occur, due not only to the fact
that curators are notoriously possessive of
the specimens under their care, but in some
of the United States there are laws
constraining the transfer from a state of
the property of private, but state-chartered
museums.

Whether or not such concentrations ever take
place, new space-saving techniques are still
needed. Even with such space-age devices as
interconnected computer networks capable of
transmitting three-dimensional holograms of
specimens, there is still no substitute for
the object itself. Replicas and casts of
specimens, especially of fossils, are cer-
tainly useful in research; but only from the
actual specimen, fossil or otherwise, can
potentially limitless new knowledge of the
past be gleaned.

The ultimate responsibility of directors of
natural history museums is, therefore, the
preservation of original specimens. The
visiting public, rather than curators or
scientists who use the collections in their
research, is the principal supporting agent
in achieving this goal. From them ultima-
tely come the financial resources to sustain
the collections. To fulfill this respon-
sibility, the director must, therefore,
attract and inform the visitors not only by
exhibits, but by lectures, tours, guidebooks
and other appropriate activities.

The director's role is therefore a double
one: first, to keep the data bank current,
second to attract public support for the
museum to accomplish its task to read the
past through its collections. The two roles
are equally important for it would be
irresponsible merely to increase the
knowledge of scientists through study of the
collections without diffusing what had been
learned to the public, on whose assistance
the very existence of a natural history
museum depends.

THE PREVENTION OF DELIQUESCENCE,
EFFLORESCENCE AND HYDRATION IN MINERAL
SPECIMENS

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SUMMARY

Deliquescence is the spontaneous solution of
a mineral by atmospheric moisture.
Efflorescence is the spontaneous loss of
essential water of crystallization from a
hydrated mineral. Hydration is the
spontaneous uptake of essential water of
crystallization. A common characteristic of
all these reactions is initiation at a
specific relative humidity level.

Methods for preventing these reactions in use
today include: 1) coating with lacquers,
2) refrigeration, 3) storage in sealed
containers at the mineral $\rightleftharpoons$ solution
equilibrium relative humidity, 4) storage at
the mineral $\rightleftharpoons$ lower or mineral $\rightleftharpoons$ higher
hydrate equilibrium relative humidity, or 5)
storage at an enforced intermediate relative
humidity.

The utility of lacquers is limited by their
low efficiency as vapour barriers.
Refrigeration alone will at best slow
reaction rates so to be effective it must be
used in conjunction with another method.
Storage in sealed containers at mineral $\rightleftharpoons$
solution equilibrium conditions risks
morphological changes since the solution
phase permits ion mobility. Storage in a
sealed container at higher $\rightleftharpoons$ lower hydrate
equilibrium conditions requires perfect
hermetic sealing; this can be difficult to
achieve in practice. Storage in a sealed
container at an enforced relative humidity
requires that the stability limits of a
specimen be known with sufficient accuracy.
This method is also limited by the accuracy
with which a specific relative humidity
range can be controlled.

Although problems are associated with all
these methods, the last two (4 and 5) are
limited only by technical difficulties and
are therefore considered the most suitable
for long-term preservation of specimens.

Introduction

Although most minerals are relatively immune
to extremes in ambient relative humidity (RH)
levels, a significant number, possibly 10%,
undergo complete, distinct phase transitions
when exposed to inappropriate RH levels.
That this is the case is not surprising since
many minerals form and are preserved in
nature at a very constant water activity. In
certain other cases, minerals only appear and
can only be collected during seasons with
atmospheric conditions favourable for their
growth.

Reactions

Deliquescence

Any water soluble salt will draw moisture
from the air and with it form a solution when
the relative humidity (RH) of the air is
higher than the water activity of a saturated
solution of that salt. This action is known
as deliquescence. The extent to which a
specimen will deliquesce depends primarily on
the RH level, the duration of exposure, the
rate of air flow, the total volume of air
from which moisture can be drawn, and
characteristics of the species involved.

Deliquescence may or may not result in mineral
decomposition. Deliquescence without
decomposition generally results in rounding of
crystal edges and etching of faces. Continued
deliquescence can reduce a specimen to a mere
crust or stain in the bottom of its tray. A.
L. Parsons (1926, p.82) related one case in
which "...minasragite which had been stored
in a possibly damp basement during the summer
was represented by a green spot in the tray.."

Deliquescence with decomposition occurs with
some minerals which contain multiple anions
and/or cations. An example of this is
buetschliite ($K_2Ca(CO_3)_2$). When exposed to
moist air K_2CO_3 is leached from this mineral
leaving a powdery pseudomorph of $CaCO_3$
(Pabst, 1974).

Hydrolysis may also occur when minerals
deliquesce. Molysite ($FeCl_3$), for example,
deliquesces and reacts to form ferric
hydroxide and hydrochloric acid. Hydrolysis
can also occur when deliquescing minerals are
concomitantly oxidized, as in the case of
nantokite (CuCl) altering to paratacamite
($(Cu_2)OH)_3Cl$).

Efflorescence

Many minerals are hydrates, having a definite
amount of water as a necessary constituent.
In some species this water exerts a
significant vapour pressure at room
temperature. If the partial pressure of water
vapour in the air falls below that of water in
the mineral, water will leave the mineral.
This spontaneous loss of water is known as
efflorescence. In most cases this will
necessitate a change in crystal structure
causing the specimen to break up into a
microcrystalline or amorphous powder.
Because dehydration occurs not only at the
visible surface but also along microscopic
and submicroscopic fractures,
intercrystalline boundaries, and even along
planes of weakness within crystals, only a
small percentage of the mineral's water need
be given off before the specimen is completely
decrepitated. In some cases, such as borax
($Na_2B_4O_7 \cdot 10H_2O$) dehydrating to tincalconite
($Na_2B_4O_7 \cdot 5H_2O$), the resulting powder is
cohesive enough that the specimen's original
form is retained. In other cases, such as
chalcanthite ($CuSO_4 \cdot 5H_2O$) dehydrating to
bonatite ($CuSO_4 \cdot 3H_2O$), there is a complete
loss of cohesive strength, and the specimen
falls to a formless mass of powder.

Hydration

Hydration is the opposite of efflorescence.
It is the spontaneous intake of water from
the atmosphere to form a higher hydrate.
Common examples of hydration include leonite
($K_2Mg(SO_4)_2 \cdot 4H_2O$) hydrating to picromerite
($K_2Mg(SO_4)_2 \cdot 6H_2O$), and hexahydrite
($MgSO_4 \cdot 6H_2O$) hydrating to epsomite
($MgSO_4 \cdot 7H_2O$).

Preservation

The fact that these reactions involve simple, distinct phase transitions permits accurate determinations and clear definitions of stability ranges. Figure 1 shows stability ranges for several mineral species and combinations of species. It is clear that there is no single RH level which, if maintained in a collection area, would suffice for the preservation of all mineral species. The consequence of this is that many of these RH sensitive mineral specimens must be preserved individually.

Lacquers

Lacquers are essentially form-fitting containers. The problem with lacquers is that all lacquers are somewhat permeable to water vapour, so that even a perfectly continuous coating will not protect a specimen from long exposures to inappropriate humidity levels.

Still, lacquers can be useful for protecting display specimens from brief exposures to inappropriate RH levels and for consolidating specimens which have effloresced.

Refrigeration

Refrigeration will slow most reactions, but unless the conditions within the refrigerator and the stability range of the specimen at the enforced temperature are known, true stabilization of the specimen would only be fortuitous. In fact it is possible that in some cases a new problem may be introduced, that is the specimen may be made unstable with respect to a phase which does not occur at room temperature.

Refrigeration may be useful in conjunction with sealed containers or enforced microclimates, but thought must be given to the conditions that will exist in the container after it has been cooled.

Mineral $\rightleftharpoons$ Saturated Solution Storage

Storing a specimen in equilibrium with its saturated solution is not advisable since the solution phase permits ion mobility. This will lead to changes in crystal morphology which can be considerable. A less common but even more serious problem is that certain minerals are subject to oxidation and/or hydrolysis while in solution.

Mineral $\rightleftharpoons$ Higher or Lower Hydrate Storage

To store a specimen at hydrate pair equilibrium conditions you would simply seal a dry specimen in a container. Dry in this sense means lacking any deliquesced water. Assume for example, that a mirabilite is sealed in a container at an ambient RH of 50%. The mirabilite will effloresce producing thenardite and water vapour until the RH within the container has risen to 75% (the equilibrium RH for the reaction mirabilite $\rightleftharpoons$ thenardite & water vapour at 20°C). This is not very taxing on the specimen, in this case only 8 μg of mirabilite will effloresce for every mL of air space.

The problem with this method is that perfect hermetic seals are difficult to achieve in practice and any loss of water vapour must be made up for by the efflorescence of more of the hydrate. Very small specimens or specimens in powder form can easily be sealed hermetically in glass ampoules, but for specimens much larger than 1 cm across this is not practicable.

Enforced Microclimates

In the methods discussed so far the specimen has been in dynamic equilibrium with another phase. A common disadvantage of these methods is that the mineral must be involved in a reaction to offset any gain or loss of water vapour (and perhaps, any change in RH brought on by temperature fluctuation). This diasdvantage is not present if the specimen is stored in the RH range between phase boundaries.
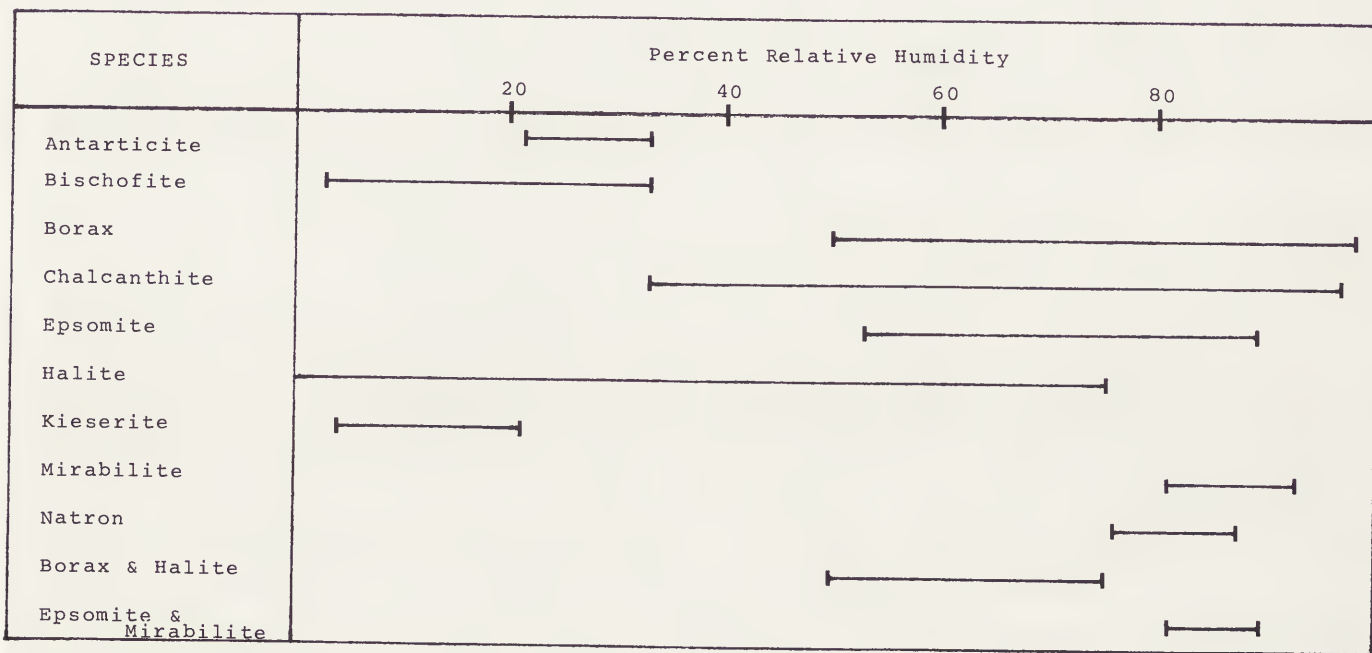

Figure 1   Approximate stability ranges for selected mineral species at room temperature.

To accomplish this a substance or mixture that will enforce an appropriate RH level must be enclosed in the container with the specimen. The mixtures commonly used in laboratories for the static control of humidity are saturated solutions, solutions of strong electrolytes, and salt hydrate pairs. The use of these in close proximity to mineral specimens is precluded by the risk of specimen contamination. Silica gel used for the static control of humidity has the advantages of being totally inert and dry to touch (Lafontaine).

In order to store a specimen at an enforced RH the stability limits of the specimen must be known. This necessitates a knowledge of both the mineralogical composition of the specimen and the stability limits of all the humidity sensitive minerals that are present. The importance of recognizing the presence of all humidity sensitive minerals in a specimen cannot be over emphasized. The alteration of even a very minor constituent can result in essentially total destruction of a specimen.

Stability limits for a number of mineral species have been collected by Waller (1980), others might be found by a search of the chemical literature, but many will require new measurements. Methods for the determination of equilibrium vapour pressures can be found in most standard physical chemistry texts.

In practice, a quantity of silica gel is conditioned to an RH near the middle of the specimen's stability range and is enclosed in a container with the specimen. If it is suspected that the specimen will absorb or desorb a significant amount of water at this RH, then it is advisable to condition the specimen as well as the gel to the desired RH. Because the containers employed are generally small, and because silica gel is being used to enforce and not merely buffer a certain RH, the amount of silica gel used for a given volume can and should be much greater than the 20 Kg m^{-3} commonly recommended for buffering display cases, (Thomson, 1977; Brimblecombe and Ramer, 1983). Amounts as high as 400 Kg m^{-3} can be used and will result in a longer maintenance-free lifetime for the container. Employing the most appropriate type of silica gel considering the RH level to be enforced (Weintraub, 1981) can have an even greater effect on this lifetime.

During assembly of the enforced microclimate a sample of the conditioned silica gel should be used to determine its useful moisture capacity. This can be done by conditioning the carefully weighed sample to an RH near the stability limit of the specimen. The weight loss or gain divided by the original sample weight and multiplied by the weight of conditioned silica gel to be enclosed in the container will give the maximum permissible loss or gain from the finished container. Containers should be weighed annually and reconstructed when the calculated maximum permissible weight loss or gain has occurred.

Because these containers are necessarily well sealed they will efficiently contain any pollutants which may be generated or released by enclosed materials (Padfield et. al. 1982). For this reason care must be exercised in selecting sealants, specimen supports, etc. In addition, organic materials will support mould growth, and

hence should not be used within a container when the enforced RH is higher than 70%.

A more detailed description of the preparation of enforced microclimates for mineral specimen preservation is being prepared.

Conclusion

Of all the preservation methods considered only storage in a hermetically sealed container at a hydrate pair equilibrium relative humidity or in a reasonably well sealed container at an enforced RH is suitable for the long term preservation of specimens. Specimens with narrow stability ranges and relatively small specimens are best preserved at a hydrate transition equilibrium relative humidity in a hermetically sealed container. Larger specimens for which perfectly sealed containers are difficult to construct are best stored in a suitable enforced microclimate.

Acknowledgements

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Section 14

Graphic and Photographic Documents

Documents graphiques et photographiques

DOCUMENTS GRAPHIQUES ET PHOTOGRAPHIQUES

Coordinateur : F. FLIEDER (France)

Coordinateur-adjoint : J. HOFENK de GRAAF (Pays-Bas)

Membres : O.P. AGRAWAL (Inde)
 J.M. ARNOULT (France)
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 M.G. BLANK (U.R.S.S.)
 H. BURGESS (Canada)
 C. CHAHINE (France)
 E.R. ELGUEZABAL BLANCO (Mexique)
 R. FELLER (U.S.A.)
 M. GILLET (France)
 K. HENDRIKS (Canada)
 Ju. P. NYUKSHA (U.R.S.S.)
 V. RADOSAVLJEVIC (Yougoslavie)
 W. ROELOFS (Pays-Bas)
 V. VINAS (Espagne)
 M.V. YUSUPOVA (U.R.S.S.)
 M. ZAPPALA (Italie)

Programme de travail 1981-1984

1. Etude du comportement chimique des fibres cellulo-
siques traitées par des agents de blanchiment et
de désacidification (BLANK, BURGESS, FELLER)

2. Analyse des différents types de jaunissement des
livres imprimés avant 1800 (HOFENK de GRAAFF)

3. Le problème de la résistance microbiologique des
papiers (NYUSKA)

4. La conservation des cuirs et des parchemins :
assouplissement, nettoyage, assèchement, protection
contre la pollution atmosphérique (BURGESS, CHAHINE
YUSUPOVA)

5. Les enluminures de manuscrits : effets des enzymes
et des fixatifs ; analyse des liants (BURGESS,
FLIEDER, ROELOFS, ZAPPALA)

6. La détérioration des papiers et des parchemins par
les pigments verts contenant du cuivre (BANIK)

7. Recherche sur la restauration et la conservation de
l'Evangile de Miroslav (RADOSAVLJEVIC)

8. La restauration des peintures chinoises sur papier
et sur soie (ELGUEZABAL)

9. La restauration des manuscrits sur feuille de pal-
mier et écorce de bouleau (AGRAWAL)

10. Le traitement de masse des livres imprimés au Cen-
tre de Sablé de la Bibliothèque Nationale (ARNOULT)

11. La stabilité des phototypes modernes et leur conser-
vation (GILLET, HENDRIKS)

12. La restauration, par des procédés chimiques, des
photographies gélatino-argentiques et des papiers
salés (GILLET, HENDRIKS)

Ce programme, établi par l'ensemble des membres, lors
de la dernière réunion de notre groupe de travail à
Ottawa, a été suivi dans ses grandes lignes.

Malheureusement, deux articles relatifs à des problèmes
de restauration fort intéressants (points 7 et 8) ne
sont pas publiés, l'un n'a pu être rédigé dans les dé-
lais, l'autre porte sur un travail qui n'a pas été ache-
vé par manque de crédit.

Des problèmes financiers ont également retardé l'instal-
lation industrielle de désacidification de masse des
documents qui devait être faite à la Bibliothèque Na-
tionale de Paris, dans son Centre de Sablé, celle-ci
est programmée pour l'année 1984.

Je signalerai, en outre, que plusieurs membres de notre
groupe se sont préoccupés parallèlement du comportement
vis-à-vis de la pollution atmosphérique, de papiers de
différentes qualités traités par plusieurs agents de
désacidification. Ces premiers essais ne sont pas encore
suffisamment avancés pour pouvoir tirer des conclusions
significatives ; ils feront sans doute l'objet d'une
séance d'affichage lors de la Conférence.

Enfin, l'étude sur les fixatifs des tracés pulvérulents
venant d'être éditée en France, ne pouvait donc être
présentée dans le cadre de l'I.C.O.M.

Parmi les communications qui figurent dans ces actes,
celles concernant les documents graphiques se répartis-
sent selon trois thèmes : Analyse - Conservation -
Restauration.

Plusieurs procédés ont été utilisés pour *l'analyse des
documents* : la réflectographie infra-rouge pour l'examen
des oeuvres d'art sur papier ; la microsonde Raman pour
l'identification des pigments des manuscrits ornés.
L'utilisation de la microscopie électronique à balayage
pour l'observation des parchemins a débouché sur une
recherche nouvelle et originale.

La micrographie a permis de déceler la nature de cer-
tains supports de Codex mexicains. On trouvera enfin
une description détaillée des dosages chimiques permet-
tant de mettre en évidence les différents produits sou-
frés présents dans les parchemins détériorés.

Divers *problèmes de conservation* sont abordés. On passe
en effet en revue la stabilisation des papiers par éli-
mination des ions métalliques ainsi que leur protection
vis-à-vis des agents biologiques. Une méthode d'assèche-
ment des cuirs est proposée ainsi qu'une expérimentation
sur le blanchiment et la transparence des parchemins.

Les travaux de restauration sont malheureusement très
restreints ; seule une communication porte sur le trai-
tement des manuscrits sur écorce de bouleau.

Pour les matériaux photographiques, l'accent a été mis
sur les problèmes de leur restauration, tout particuliè-
rement pour les daguerréotypes, les papiers salés ainsi
que pour les photographies noir et blanc dont l'image
est pâlie.

CONSERVATION AND STUDY OF THE PROPERTIES OF BIRCH-BARK

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SUMMARY

With time, the birch-bark which was used for writing in ancient India becomes very fragile. Not only its constituent layers separate out but the material also becomes weak. Lamination between two sheets of Mowilith coated chiffon have given good results for strengthening.

In order to understand the nature of the material, some fundamental properties of birch-bark have been studied. Effect of acids and alkalies was also examined. Dilute alkaline solutions seem to deteriorate the birch-bark more than the acid solutions.

PART I CONSERVATION OF A MANUSCRIPT

INTRODUCTION

In course of time, birch-bark sheets which were commonly used in ancient India for writing, before paper was known, become extremely weak and fragile. The bound manuscripts, particularly suffer because the folds in the birch-bark tend to break.

As was noted earlier also, the birch-bark is composed of several layers. These layers separate out from each other. The material is also weakened considerably.

A birch-bark manuscript was received in our Laboratory for treatment sometimes back. It was in a very bad state of repair.

CONDITION OF THE MANUSCRIPT

The birch-bark sheets were highly deteriorated and had become very fragile due to age or because of lack of proper maintenance. Sheets were stiff, brittle and were gradually disintegrating and falling to pieces. In many a case layers were separating. We found that there were tears in the sheets. Stains and spots could also be noticed in several of them.

Earlier, on some sheets, paper strips were pasted for repair.

Insect activities were noticed but mostly limited to the paper strips used earlier for repair work. Normally birch-bark is not attacked by insects.

INK

Black carbon ink had been used for writing. This ink was practically insoluble in water, methanol, acetone and benzene.

DETERIORATION

The main types of deterioration can be summarized as follows :

i.   Loss of flexibility
ii.   Separation of individual layers of birch-bark
iii. Darkening of the birch-bark
iv.   Presence of stains and spots

CONSIDERATIONS FOR CONSERVATION

There are several considerations for conservation of birch-bark manuscripts. The main are :

i.   Imparting of flexibility to the material.
ii.   Fixing the separating layers together in a manner that the flexibility is not impaired. Simultaneously, the material used for adhering has to be such which does not impart any colour of its own and does not change the basic properties of birch-bark.
iii. Removal of stains and spots from the surface of the bark.
iv.   Repairing the torn sheets.
v.   Strengthening of individual sheets by providing additional support.

The manuscript in question was bound and that posed further problem because at the bend the birch-bark becomes weak and unless proper strength could be given, it was not possible to bind the sheets together once again.

CLEANING

It was noticed that organic solvents, like ether, acetone, benzene or toluene used for cleaning produce a white appearance. Possibly this is because of the solubility of a portion of birch-bark in the solvent. We tried a methanol:water mixture (50:50) mixed with a few drops of glycerine. This mixture gave good results. Methanol also produced slight white spots but addition of glycerine avoided this phenomenon.

Dark or smoky bark sheets are cleaned with trichloroethane.

FLEXIBILITY

For imparting flexibility we tried application of a 5% solution of glycerine in alcohol mixed with pentachlorophenol to the extent of 1%. This solution did not give encouraging results.

A 5% solution of PEG 400 in water was also tested. The leaves were kept for 2-3 hours in a bath of this mixture, taken out and dried. For drying, the birch-bark was kept inbetween blotting papers, over which a light weight was kept. There was some improvement but there is further scope of work in this direction.

REPAIR AND STRENGTHENING

While selecting the techniques for repair of these manuscripts there were several considerations :

i. Inserting a tissue paper or a fresh sheet of birch-bark inbetween the individual layers of birch-bark.

ii. Lamination between 2 sheets of cellulose acetate with solvent technique.

iii. Lamination between 2 sheets of a transparent material, like chiffon coated with a polymer resin.

Inserting tissue paper

Trials were made for inserting a tissue paper inbetween the two layers of the bark using starch paste. For application of this technique it was necessary to separate the loose layers of the bark completely so that the tissue paper or a new sheet of birch-bark could be pasted. Several problems were encountered for successful implementation of the method. The main were :

i. Separation of layers was difficult because the individual sheet was rather fragile and brittle. The knots in the bark make separation still more problematic.

ii. Flexibility of the sheets is not increased.

iii. The process takes a long time and a good deal of labour is involved.

For these reasons, the process was not used for this manuscript.

LAMINATION BETWEEN CELLULOSE ACETATE SHEETS

The birch-bark was placed between tissue paper and cellulose acetate foils. Fixing was done with acetone with the usual solvent process of lamination. With this process, the sheet became whitish, possibly because of the solvent action of acetone. The visibility of writing was also reduced to some extent. Visibility was reduced even when the cellulose acetate foils were applied by heat mounting. Furthermore, flexibility was not as much as was desirable.

HEAT SEALING WITH CHIFFON

One of the processes of repair of paper manuscripts is application of chiffon, normally with starch paste or CMC paste. Because the starch paste does not go very well with the birch-bark we thought of using Mowilith (a Hoescht product). Trials were made with 20, 25, 30, 35 and 40% Mowilith solutions. The solution was coated on chiffon cloth by brush in a thin film. It was allowed to dry and then used for sealing the birch-bark inbetween. The birch-bark was kept between coated chiffon which in turn was placed between silicon papers. Heat was applied first with heating press and later inside the dry mounting press. 30-35% Mowilith film at a temperature of 70-75°C for 2 to 5 minutes gave very good results.

With this method of lamination, the following advantages were observed :

i. Flexibility is maintained.

ii. Very good visibility is retained compared to cellulose acetate lamination.

iii. The method is reversible.

iv. The process is easy and quick.

v. All the materials are available in India.

The individual layers of birch-bark which were separating were first fixed together with a thin solution of CMC paste before application of chiffon.

When all the sheets have been repaired they will be bound together in the usual manner. We are considering this technique as a tentative one and have applied it considering the very bad state of the manuscript in question. It was falling apart and an immediate action was called for.

PART II STUDY OF PROPERTIES

Although the above manuscript was treated in the manner described above, certain fundamental questions remain unanswered. Some studies on birch-bark manuscripts were reported earlier[1]. The work reported here is further to that.

EXPERIMENTAL

Nature of Sample

We obtained a sample in the form of a long bark measuring around 70x30 sq.cm. It was yellowish in colour with a number of nodes vertically present on the bark. The colour of the nodes was slightly dark brown or of brick colour. The inner surface of the bark was white.

Sampling

It was considered likely that the nodes and the inter-nodes might have different properties, as such samples were prepared into two different portions :

i. Nodes, and

ii. Inter-nodes (or without nodes)

The nodes were separated by cutting with the help of a pair of scissors.

Physical Properties

The number of nodes present per square meter area of the birch-bark were counted. In this particular case, they numbered about 3500 /sq. meter. The length of the nodes were measured with the help of a scale and the numbers in the ranges of 10-20 mm, 20-30 mm and so on were counted. The average length of the nodes was found to be 12 mm to 93 mm in the respective ranges (Table 1). The width averaged between 1-5 mm.

Grammage (Basic Weight)

The average basic weight of the birch-bark was found to be 47.37 gms/m^2.

i. Thickness (4 layers) : 0.37 mm

ii. Density : 5.1 g/m^3

iii. Bulk : 0.19 cm^3/gm

Strength

Tear index, burst index and folding endurance of birch-bark, before ageing and

after ageing for 48 hours at 105°C were determined. It is found that there is a sharp fall in the strength of birch-bark after ageing (Table II).

The material had become so weak that it was not possible to measure the tear index and the bursting strength. The folding endurance dropped from 7.21 to 1.118 at 0.5 kg tension.

Ash Content

Samples of nodes and inter-nodes about 2 gm each were taken for determination of ash content. They were kept in the furnace and heated upto $925 \pm 20°C$ temperature.

Observations were made at regular intervals. Samples were kept in the furnace at 300°C. Burning started within 5 minutes, emitting smoke which was having a peculiar odour like that of camphor.

At this stage, the ash was black grey in colour. At 500°C the samples was almost completely burnt and the volume of the black residue was reduced.

At 700°C the sample was completely burnt leaving no trace of carbon. The colour of the ash at this stage was brick-red. The sample was weighed and the percentage determined to around 0.298% (0.3%).

The sample was again heated to 900°C and there was no change noticed either in the appearance or in the weight of the sample.

The above results were similar in the case of nodes and anti-nodes except that the colour of the ash of the inter-nodes was blakish brick like.

Chemical Properties

Properties, like moisture content, inorganic content, pH (acidity) and copper number (reducing groups) were carried out by standard procedures.

Silica, iron and traces of several metals were found through analysis of ash with the help of spectrophotometer, atomic absorption and X-ray fluorescence method (Table III).

The pH was determined by titration according to TAPPI method given for paper.

Cellulose and lignin were also determined in the lots of bark samples. The results can fluctuate according to the samples. Lignin was determined separately in the portion of bark of lenticels and without lenticels. Lenticels were found to be lignified than the rest of the portion of bark (Table III).

The solubility of bark was carried out in water, alkali, acid and organic solvents. Most of the portion of bark is dissolved in organic solvent (Table IV).

CONCLUSION

These studies are to be further continued for understanding fully the nature of birch-bark, how it deteriorates and what can be done to stop the process of deterioration.

REFERENCES

1. AGRAWAL, O.P., BHATIA, S.K., Investigations for Preservation of Birch-bark Manuscripts, ICOM Committee for Conservation, 6th Triennial Meeting, Ottawa, 1981, 81/14/18.

TABLE-I

1. a) Length of Lenticels on bark :

Range	Aveg. Length, mm
10-20	12
21-30	25
31-40	37
41-50	46
51-60	54
61-70	64
71-80	76
81-90	82
91-100	93

b) Width of Lenticels, mm

Minimum	Maximum
1-1.5	4-5

TABLE-II

Strength Properties of Birch-Bark

Grammage (Basic Wt.), g/m²	:	47.37
R. Humidity %	:	56
Temperature °C	:	30

Sample	Tensile index N.m/g	Stretch %	Tear index mN.m²/g	Burst index K.Pa m²/g	Folds at 0.5 kg	Thickness micr ons	Density g/cm³	Bulk cm³/g.
Before ageing	Nil	Nil	4.56	3.93	721 (4 layers)	37.2	5.1	0.19
After ageing	Nil	Nil	Nil	118	"	"	"	

TABLE -III

Chemical Properties of Birch-Bark

S.No.			Before ageing	After ageing
1.	Copper Number	:	2.53	(12,24&48 hrs.)
2.	pH of extractive of paper	:	5.6,6.3(hot)	2.99,3.67,3.82
3.	Acidity, %	:	0.17	
4.	Sizing material	:	-	
5.	Coatings	:	-	
6.	Colour or dyes	:	Natural brownish colour	
7.	Ash, %	:	0.3	
8.	Silica	:	0.029	
9.	Acid insoluble lignin,%	:	5.48	Lenticels W.cels (0.64 3.32)
10.	Cellulose, %	:	38	
11.	Moisture, %	:	4.33	
12.	Inorganic content		Lenticels Without cels	
	a) Iron	:	2.9 0.89	
	b) Traces of Cu, Mg, Mn, Ti and Na observed through ash analysis by atomic absorption and x-ray fluorescence method.			

TABLE-IV

Solubility of Birch-Bark

S.No.	Solvents	Solubility %	Colour Reversion
1.	Cold water	Nil	No change
2.	Hot water	4.37	"
3.	1% NaOH	10.20	-
4.	1% HCl	0.6	Nil
5.	Acetone	17.45	Faded
6.	Benzene	14.60	Reddish
7.	Chloroform	19.8	Whitish
8.	Carbon Tetrachloride	9.76	No change
9.	Ethanol	22.00	Whitish
10.	Ether	20.50	Yellowish
11.	Xylene	14.97	Nil, but shrinkage

TABLE-V

Effect of acids and alkalies on texture, colour and folds of bark

Acids and alkalies	Folds at 500 gms. 2%	Folds at 500 gms. 5%	Change in Texture 2%	Change in Texture 5%	Change in Colour 2%	Change in Colour 5%
Hydrochloric acid	499	213	Nil	Nil	Nil	Nil
Acetic acid	1200		Nil	Nil		
Oxalic acid	1100	More elasticity	--Shrinkage--		Nil	Nil
Sodium Hydroxide	Nil	Nil	More portion dissolved		Bark dissolved	
Sodium carbonate	22	Nil	Elasticity increased		Colour changes of Lenticels brownish to dark brown	
Cal.hydroxide	38	14	--Shrinkage--		Nil	Nil

CHEMICAL CHARACTERIZATION OF PARCHMENT, PART I SULFUR-BEARING CONSTITUENTS

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SUMMARY

Investigation of parchment samples by means of x-ray fluorescence and combustion analysis in all cases reveals noticeable portions of sulfur. It therefore seems to be justified to take into consideration sulfur-bearing substituents as possible binding-sites for transition metal ions in the course of pigment-induced degradation of parchment. In order to clarify this question samples of decayed parchment as well as undamaged parchment of contemporary origin were analyzed with respect to their contents of sulfhydryl- and disulfide groups as well as sulfate stemming from acid glycosaminoglycans (GAGs) of the ground substance of connective tissue. Sulfate was estimated by turbidimetric measurement after separation of GAGs from the proteinaceous portion of parchment. Sulfhydryl- and disulfide groups were titrated amperometrically after reductive treatment of the samples by sodium borohydride. It could be shown that sulfhydryl- and disulfide sulfur without exception represents the main portion of sulfur in parchment whereas sulfate from acid GAGs is present only in minimal amounts.

INTRODUCTION

It is undoubted that an essential prerequisite for successful restoration of parchment for conservation purposes would be a profound knowledge of its properties in their context with chemistry and structure. Unfortunately these properties are highly variable due to the fact that parchments are of biological origin and therefore depend strongly on such factors as animal species, age, sex, as well as nutritional influences. Up to now there are no physical or chemical methods at hand allowing some standardization which could be applied generally. Nonetheless a clarification of the reaction mechanisms in the course of degradative processes of parchment seems to be imperative, especially in the case of damage caused by the action of transition metal ions contained in various pigments for illuminating purposes as well as in certain inks. Furthermore, the influence of atmospheric pollutants such as gaseous sulfur dioxide in combination with metal-containing dust where iron could be a main constituent should not be underestimated.
In the course of our investigations concerning the destructive action of copper-containing pigments on carrier materials such as paper and parchment ("Kupferfraß") a first approach has been made in that possible binding or reaction sites for metal ions within the complex structure of parchment were to be detected and estimated quantitatively. Our consideration on this point was that binding of metal ions to certain functional groups or their reaction with stabilizing crosslinks would result in heavy structural disturbances thus paving the way for reactions leading to a further breakdown of parchment structure. Regarding the macromolecular composition of parchment consisting mainly of a fibre-network formed by collagen fibrils with minor and varying portions of the so-called ground substance the conclusion is obvious that disulfide crosslinks of αl-type III collagens as well as sulphate groups of acid glycosaminoglycans (GAGs) can be reaction and binding sites for transition metal ions, respectively. It should be mentioned in this context that the reductive cleavage of disulfide bonds in presence of i.e. copper ions leads to the formation of exceptionally stable copper mercaptides. Though there is stated in the literature (STIMlER & TANZER 1) that in contrast to most other naturally occurring crosslinked proteins the most abundant types of collagen are devoid of disulfide bridges a certain amount of disulfide-containing is likely to be encountered in parchments. The aim of our work described in the following was therefore to estimate the amounts of disulfide groups and free sulfhydryl groups, respectively, as well as the amounts of sulfate groups bound to the acidic GAGs of various parchment samples. Moreover it had to be kept in mind that leather as well as parchment are capable of absorbing sulfur dioxide from the atmosphere leading to as much as 5.0-8.0 % sulfuric acid as reported for rotted leathers (HAINES 2). The estimation of total sulfur was therefore also carried out in the course of our work.

EXPERIMENTAL

The parchment samples at our disposal were of different origin and state of preservation. Samples of fresh and untreated parchment were compared to samples taken from aged objects being kept under varying environmental conditions. For details see also explanations to Table 1.

Total sulfur was estimated by fusing the acetone defatted samples with metallic potassium and conversion of the generated sulfide to hydrogen sulfide by the addition of hydrochloric acid. The liberated hydrogen sulfide then reacted with cadmium acetate to form cadmium sulfide which in turn was titrated iodometrically in presence of hydrochloric acid.

Free sulfhydryl groups were estimated by means of amperometric titration of solubilized parchment samples with silver nitrate in 8M urea according to the method of HAMM & HOFMANN (3) modified by STACHELBERGER (4).

Disulfide groups were also estimated amperometrically after reductive solubilization of the samples in sodium borohydride-containing 8M urea. The amount of

disulfide groups results from subtraction of free sulfhydryl groups from total sulfhydryl after reduction.

Acid glycosaminoglycans (GAGs) were separated from proteinaceous material by papain digestion and fractionated by using potassium acetate and cetylpyridiniumchloride (CPC) according to KLEIN (5). Sulfate groups were estimated by nephelometric measurement of precipitated barium sulfate after hydrolysis of GAGs with 3N HCl. Hexosamines were detected with Ehrlich`s reagent (BOAS 6) and uronic acids by carbazole-borate reaction (BITTER & MUIR 7).

Methionine (D-2-Amino-4-(methylthio)butanoic acid), an important sulfur-containing amino acid, was determined quantitatively in a few samples by taking the amino acid profile of the samples after hydrolysis and subsequent ion exchange of chromatography.

RESULTS AND DISCUSSION

The analytical results concerning the portion of acid glycosaminoglycans (GAGs) generally show that the ground substance of connective tissue contributes only to a minimal degree to the amount of functional groups being capable to react with metal ions. The sulfate content (appr. 0,01 mmoles per 100 gr. parchment) as well as the hexosamine and uronic acid contents (appr. 0,02 mmoles per 100 gr. parchment) are close to their detection limits. Sulfate as well as carboxylic groups bound to GAGs should therefore be negligible with respect to metal cation binding.

The methionine contents have been determined in samples of goatskin and sheepskin parchments (samples no.6 and 9; see Table 1) and have been found to be identical within the limits of error. The portions were 4 mmoles per 100 gr. of parchment. Methionine sulfur therefore represents a considerable but more or less constant portion within the amount of total sulfur.

Table 1 gives a survey of our results achieved so far. It can be seen that total sulfur in new and untreated parchments amounts to between 10,9 and 14,4 mmoles per 100 gr.parchment. The difference between total sulfur and the sum of disulfide, sulfhydryl and methionine sulfur is comparatively low in new parchments and is minimal in sample no.6 (goatskin parchment). In strongly aged samples which presumably were exposed to highly deleterious environmental conditions including intensive sunlight the values for total sulfur have a maximum. Parts of these very objects which had obviously better protection show values much lower. It seems evident that a high degree of damage goes along with high values for total sulfur but at the same time it has to be noted that disulfide and sulfhydryl sulfur being present in most of the samples (19,6 to 47,4% of total sulfur in new samples) decreases strongly in damaged samples. In sample no.5 taken from a heavily darkened back of a book binding there is no disulfide and sulfhydryl sulfur any more compared to sample no.4 taken from the considerably lighter cover which has been protected from light and other atmospheric influences. This fact could at least be partly explained by the formation of S-sulpho groups arising from the reaction of disulfide groups with sulfite ions formed in the course of incorporation of atmospheric pollutants such as sulfur dioxide. Binding of metal contaminants contained in dust to form metal mercaptides could also contribute to the loss of estimable sulfhydryl and disulfide, respectively.

From our results the conclusion can be drawn that in parchment disulfide as well as free sulfhydryl groups can occur in considerable quantities thus representing possible binding sites for transition metal ions. But at the very moment attention should be drawn on the fact that in aged and highly damaged parchment total sulfur reaches a maximum whilst disulfide and sulfhydryl sulfur decrease considerably. Some thought could be given to the possibility that the values of total sulfur in parchments as well as disulfide and sulfhydryl sulfur could be useful parameters for the assessment of the degree of damage parchment samples have undergone but there is certainly need for further research in this field.

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Table 1

Contents of total sulfur, disulfide and sulfhydryl sulfur (mmoles per 100 g parchment) in the samples under investigation

Sample no.	Total S mmoles/100 gr parchment	Disulfide S		Sulfhydryl S	
		mmoles/ 100 gr parchment	% of total S	mmoles/ 100 gr parchment	% of total S
1	11,9	(-)		2,34	19,6
2	18,4	0,62	3,4	1,56	8,5
3	28,4	(-)		2,5	8,8
4	17,8	1,25	7,0	0,31	1,7
5	31,2	(-)		(-)	
6	10,9	5,0	45,9	0,94	8,6
7	16,8	3,1	18,45	1,25	7,4
8	11,5	0,62	4,9	1,88	15,0
9	14,4	6,25	43,4	0,62	4,0
10	30,0	1,56	5,2	1,88	6,0

(-) not detectable

Samples under investigation:

Sample no.1: Calfskin new no.9 *
Sample no.2: Calfskin old, well preserved; without ink writing +
Sample no.3: as no.2, with ink writing +
Sample no.4: Calfskin old, cover of bookbinding, lightly colored, well preserved +
Sample no.5: Calfskin old, back of the same object as no.4, heavily darkened, extremely stiff +
Sample no.6: Goatskin new *
Sample no.7: Goatskin old, thin, very stiff +
Sample no.8: Goatskin new, sample taken from the edge of the pelt, stiff +
Sample no.9: Sheepskin new *
Sample no.10:Sheepskin old, from bookbinding, stiff +

* Samples supplied by: Messrs. Carl Wildbrett, D-8903 Bobingen, FRG
+ Samples supplied by: Österr.Nationalbibliothek, Vienna, Austria

DAGUERREOTYPE: A PRECAUTIONARY DISCUSSION OF
DETERIORATION, CLEANING AND TREATMENT

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SUMMARY

As part of the research for the exhibition,
"Robert Cornelius: Portraits from the Dawn of
Photography" (20 October 1983 - 22 January 1984,
National Portrait Gallery, Smithsonian Institution,
USA), approximately half of the extant Cornelius
daguerreotypes, as well as daguerreotypes by
Joseph Saxton and Walter Rogers Johnson, were
submitted for scientific analysis. This collection,
containing plates dating from 1839 to 1843 and
including the oldest photograph made in the United
States is the largest coherent body of the earliest
American photographic objects. While the thrust of
the analyses was to understand the working methods
of Robert Cornelius and to date the plates, this
study also presented an opportunity to examine
long-term aging and the results of past preservation
treatments on daguerreotypes of known provenance.
The varieties of corrosion products affecting
daguerreotypes were followed through the research.
In addition, the related effects of deterioration
of cover glasses and mats were observed. Further,
the characteristic deleterious consequences of both
cyanide and thiourea cleaners, as well as the
corrosion products associated with their use,
were noted. Recommendations for stabilization of
daguerreotypes pending the publication of reliable,
nondestructive cleaning methods are given.

INTRODUCTION

In the fall of 1983, the National Portrait Gallery,
Smithsonian Institution, organized an exhibition
on Robert Cornelius (1809-1893), a pioneer
Philadelphia daguerreotypist and the founder of
American portrait photography. By trade a
manufacturer of quality lighting fixtures and plated
goods, Cornelius was active as a daguerreotypist from
1839 until 1843. In the course of his career he
introduced and utilized modifications to Daguerre's
original process--notably multiple sensitization of the
plate and refined polishing techniques--which made his
daguerreotypes superior to anything contemporary to
them. The exhibition, titled "Robert Cornelius:
Portraits from the Dawn of Photography" displayed all
the known Cornelius plates, as well as daguerreotypes
by Joseph Saxton (the earliest surviving American
photograph), by Walter Rogers Johnson and by Henry
Fitz, Jr. Comprising thirty-six objects in all, this
exhibition was the largest coherent body of early
American daguerreotypes ever assembled.

As an integral part of the research for the exhibition
and catalog, sixteen of the daguerreotypes--fourteen
Cornelius's, the Saxton, and one Johnson--were
submitted for scientific analysis at the Materials
Research Laboratory, The Pennsylvania State University.
The purpose of this analysis was to document the
development of Cornelius's working methods, since his
written records have not survived and to determine a
chronology for the plates based on observable
improvements in the images' microstructures and on
chemical modifications to the original process,
specifically gilding.

The details of the scientific study are described in
the catalogue [1] of the exhibition (copies can be
obtained from the National Portrait Gallery,
Smithsonian Institution, Washington, D.C. 20560). Of
particular interest to those charged with the care of
photographs are the experimental findings associated
with the characteristic effects of both corrosion and
corrosion removal on daguerreotypes. Since the
Cornelius sample represents the largest analyzed group
of early American photographs and since the provenance
of most of these daguerreotypes is known in some detail,
these results take on a special significance.

These analyses were primarily done using Scanning
Electron Microscopy and Energy Dispersive X-Ray
Spectroscopy. It is important to note that it is
impossible to ascertain by visual inspection alone
either the chemical or physical constitution of a
daguerreian image or to positively identify daguerreo-
types that have been cleaned. Scanning Electron
Microscopy is a nondestructive tool that can be used to
obtain this kind of information. Optical microscopy
does not offer sufficient resolution to examine either
the characteristic daguerreotype image microstructure
or the damage associated with corrosion or cleaning
treatments.

Chemical data about daguerreotypes is obtained using
various forms of spectroscopy. Energy Dispersive X-Ray
Spectroscopy (EDX) is the simplest method because this
tool is usually used along with a scanning electron
microscope. EDX gives general chemical information.
For instance, the presence of gold in a daguerreotype
spectrum confirms that the daguerreotype was gilded.
However, EDX is not sensitive to lower molecular weight
elements. Thus, some corrosion products, particularly
certain tarnish films, cannot be detected using this
method. Fourier Transform Infrared Spectroscopy (FTIR)
has been used to identify tarnish films and corrosion
products which are not detected by EDX.

While chemical data is extremely important, a great deal
of information about daguerreotypes and their past
treatments can be obtained solely on the basis of
scanning electron microscopic examination. The
following secondary electron micrographs are offered as
a guide or atlas for the identification of the commonly
found types of daguerreotype corrosion and the
deleterious results from the use of the traditional
solvent cleaning treatments.

DAGUERREOTYPE MICROSTRUCTURE

Before going on to look at the corrosion on
daguerreotypes, it is important to understand the
typical characteristics of the daguerreian
microstructure. For a more detailed discussion of
microstructural conformation and alterations
attributable to processing, the reader is referred
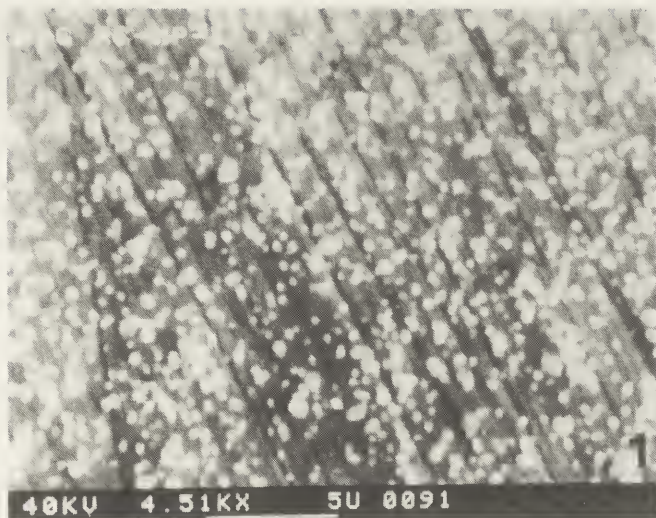elsewhere [1,2].

Figure 1 shows the highlight area of a daguerreotype. Unlike most photographic materials, the highlight areas in daguerreotypes have the greatest number of image particles. The image seen by the viewer is produced by light scattering from the image particles. These range in size over 0.1 - 1.0 μm. That is, they are on the order of the wavelengths of visible light. Highlight areas may have as many as 200,000 image particles per mm^2. The scale bar is equal to 5 μm.

Figure 2 shows a shadow area from the same daguerreotype seen in Fig. 1. In contrast to highlight areas, the shadow areas of a daguerreotype have very few shadow-particle agglomerates (50-100 per mm^2) which may range in size from 5-50 μm in diameter. The dominant imaging mode in these areas is specular reflectance off of the plate surface and away from the viewer. The scale bar is equal to 5 μm.

EFFECTS OF TRADITIONAL SOLVENT-TYPE CLEANERS

Because daguerreotypes are made on silver plate, they are subject to the formation of tarnish films. These films are primarily silver oxide and silver sulfide.

The presence of these films tends to blacken and obscure the image. Most often, tarnish has been removed using silver solvents, usually potassium cyanide and thiourea solutions. Both of these solvents etch the surface of the daguerreotype plate, and they also dissolve, break up, and rearrange the image particles. These changes result in irreparable alteration of the daguerreian image because image appearance is directly dependent upon the size and spacing of the image particles, as well as the specularity of the underlying daguerreotype plate. Further, the etching action of these traditional cleaners increases the surface area of the plate, leaving the daguerreotype more vulnerable to future corrosion.
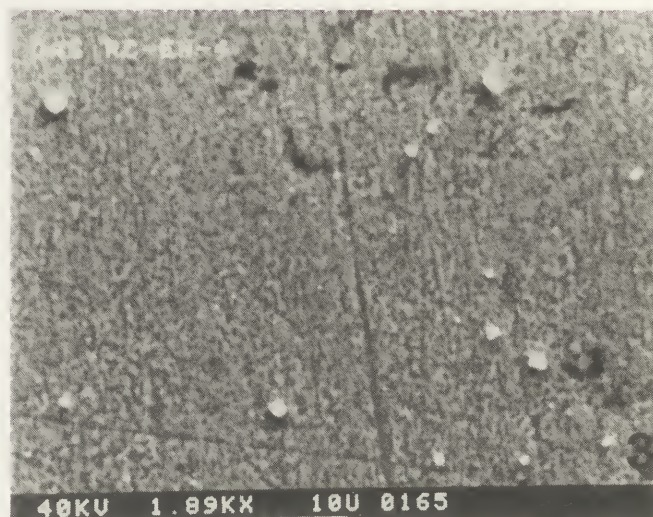

Figure 3 is typical of a shadow area from a daguerreotype cleaned in a cyanide cleaner. The small white particles are dissolved and redeposited image particles which probably originated in some other area of the daguerreotype plate. The scale bar is equal to 10 μm.

Figure 4 shows a shadow area of a daguerreotype cleaned with a thiourea cleaner. Even though the scale is different, it can be seen that the overall etching and image particle dissolution is less severe than that seen in Fig. 3. The scale bar is equal to 5 μm.
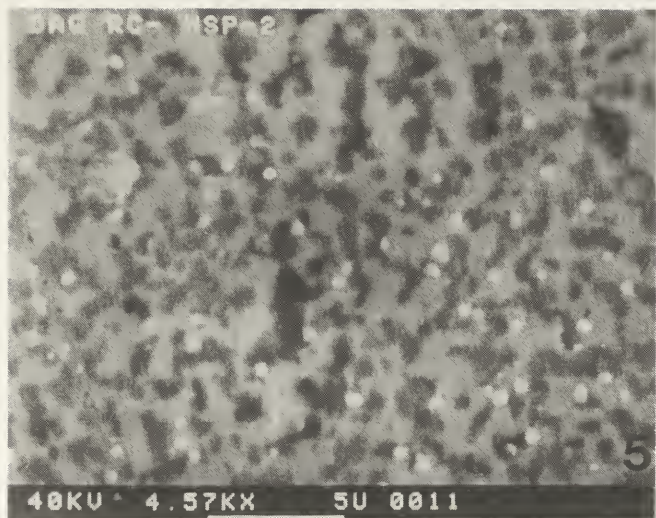
The shadow area shown in Figure 5 is examplary of a daguerreotype which has been subjected to repeated solvent cleaning treatments. The small white image particles are scattered everywhere over the plate surface. Severe etching is clearly visible. The scale marker is equal to 5 μm.

Visual examination of micrographs is sufficient to identify a previously cleaned daguerreotype. In general, a daguerreotype cleaned before 1954 can be assumed to have been cleaned in cyanide. Those cleaned after that time are more likely to have been cleaned with thiourea solutions. Etching from cyanide cleaners is more drastic than that of thiourea cleaners, but the position differentiation between these cleaners cannot be made without some chemical data. FTIR is an effective tool to identify which solution was used because both cyanide and thiourea cleaners leave corrosion films on the daguerreotype surface which are formed as a direct result of the treatment. Therefore, silver cyanide films or silver-thiourea complexes and silver phosphate films will be detected using FTIR spectroscopy. This technique will also indicate daguerreotypes which have been treated using both of these cleaners.

EVIDENCE OF CORROSION DUE TO DEVITRIFICATION OF COVER GLASSES

The glasses used as glazing materials for daguerreotypes during the nineteenth century are inherently unstable. The harm caused by these glasses is manifested in two ways. First, glass decomposition products fall off of the daguerreotype surface and initiate corrosion. Second, the deterioration of the glasses produces a highly corrosive environment which is contained and maintained within the daguerreotype package. Glass-related corrosion takes many forms from the so-called "mold growth" on daguerreotypes to certain types of etching of the plate surface. Some common effects of glass corrosion can be seen in the Cornelius sample.

Figure 6 is from the shadow area of an uncleaned daguerreotype. The diffuse etching seen as the darker overall patterning on the plate surface is from droplettes of highly alkaline solutions, probably sodium hydroxide with dissolved silicates, which fall from the cover glasses. This etching is not found uniformly distributed over the plate. Further, it is clearly not related to the more severe damage caused by solvent cleaners. It should be noted that only a very small number of nineteenth century daguerreotypes have never been cleaned. Thus, this diffuse etching is not often observed. The scale bar is equal to 5 μm.
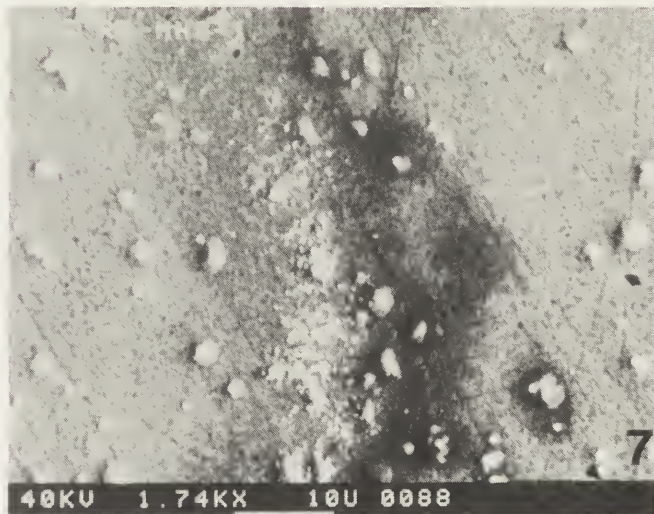
More often, glass-related etching is catastrophic and appears as deep-winding cracks in the plate surface. The darker line in the central portion of the field shown in Figure 7 shows a relatively mild example of this phenomenon. The very small, bright-white

particles just to the left of the dark line are an
example of glass decomposition products on the plate
surface. This type of catastrophic etching is commonly
observed in a variety of materials. The phenomenon
occurs where there has been etching subsequent to some
overall etching treatment. The deep etch lines appear
to be random and not controlled by grain boundaries or
other constraints. The scale bar is equal to 10 μm.
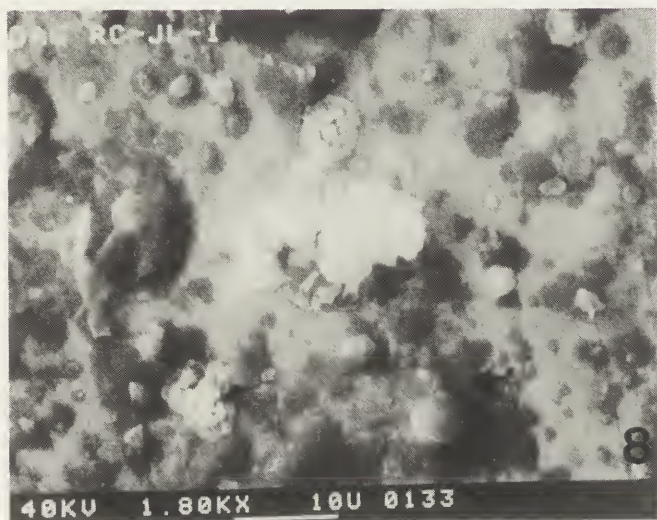
Glass decomposition products which have fallen onto
the plate surface are very easily found on
daguerreotypes. These may be "splats" of various
silicates as in the darker grey formations (a) seen
in Figure 8. The bright-white flower-like
formation (b) in the center of the field is silver
sulfide. Two shadow particle agglomerates (c) are
visible: one directly above the silver sulfide growth
and one in the lower left quadrant. A finding map is
provided as an aid in identification. The scale bar
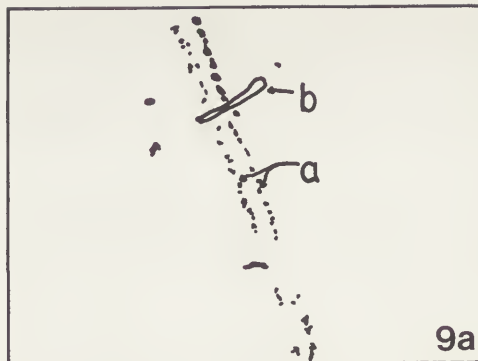is equal to 10 μm.

Figure 9 shows two lines of silver sulfide dendritic
growths (a) down the center of the field. The larger
crystal (b) lying across the lines of dendrites is a
glass stone or crystal which has fallen from the cover
glass to the daguerreotype (see finding map). The
exact chemistry of this stone was not determined.
Glass stones are easily mistaken for dust because of
their relatively large size and their silica-based
chemistry. There are about seven or eight varieties of
glass stones found both in daguerreotype cover glasses
and on daguerreotype surfaces. The scale bar is equal
to 100 μm.
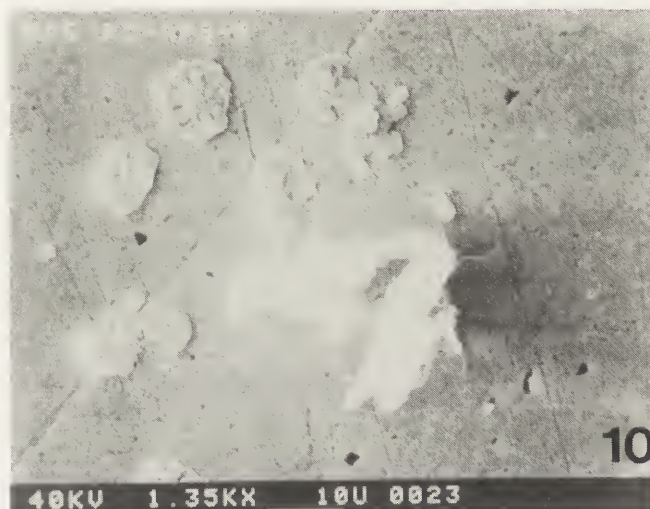
The growth in the center of Figure 10 is a silver-
sulfide silicate. Its specific chemistry was not
determined. The fibrils coming off the sides of this
growth are typical of many other silicate growths.
This daguerreotype was cleaned in thiourea. The
overall etching is very mild when compared to the
cyanide etching seen in Fig. 3. The scale bar is equal
to 10 μm.

OTHER CRYSTAL GROWTHS AND SCUMS

A variety of crystalline compounds can be found on
daguerreotypes. Usually, this type of corrosion is
associated with daguerreotypes that have already been
treated with a solvent cleaner. Crystal growth is
part of the re-corrosion process. The silver sulfide
dendrites in Fig. 9 are an example of this. These
crystals exhibit a wide variety of morphologies and
chemistries depending upon the state of the daguerreo-
type plate, the initial daguerreotype processing, the
severity and type of cleaning treatment, the extent of
glass corrosion, storage and display conditions, and
other factors. Most commonly, these crystals are
composed of silver, copper, gold, mercury, silicon,
sodium, calcium, magnesium, aluminum, lead, sulfur, and
oxygen. Of course, silver, copper, gold, and mercury
are derived from the image material and the daguerreo-
type plate. Silicon, sodium, calcium, magnesium,
aluminum, and lead come from the cover glasses. Oxygen
and water are contributed by the atmosphere. Sulfur
and chlorine may originate in the atmosphere or in the
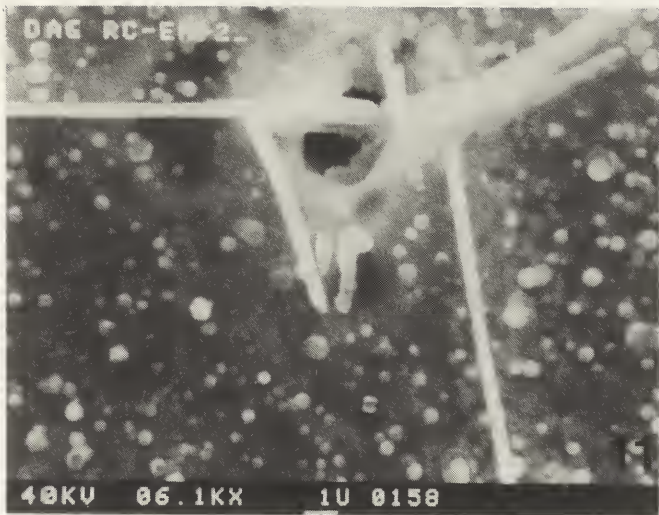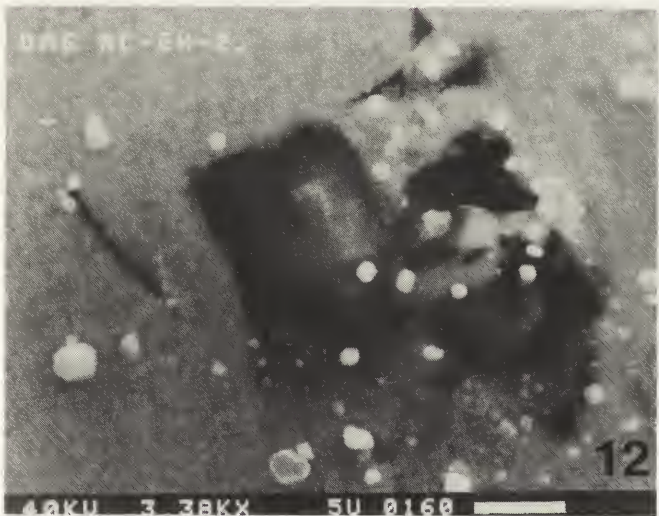cover glasses.

Figure 11 shows acicular silver sulfide growths around
an etch pit. The particulate matter in the background
is primarily a surface scum of unspecified chemistry.
The scale bar is equal to 1 µm.

Surface scums are usually amorphous coatings with
similar chemistries as the compounds above. These
scums are also found on cleaned daguerreotypes.
Figure 12 shows the scum around an etch pit. The
particles are dissolved and redeposited image particles
and, also, unspecified crystalline material that is not
part of the daguerreotype image material. The scale
bar is equal to 5 µm.

CONCLUSIONS

These twelve micrographs do not and can not represent
an exhaustive catalogue of daguerreotype corrosion.
However, they do show the most commonly observed
effects of corrosion. The destructive results from
the use of the traditional silver solvent cleaners
are readily seen in the micrographs. Some forms of
corrosion related to the deterioration of cover glasses
are also indicated. In general, the daguerreotypes
in the Cornelius sample are in fairly good condition.
The Cornelius daguerreotypes which have been cleaned,
not surprisingly, are the ones which show the most
overall corrosion. Several nondestructive methods
for cleaning daguerreotypes are being developed at the
Materials Research Laboratory of The Pennsylvania State
University. The traditional daguerreotype seal of
daguerreotype, mat, and cover glass bound together with
a paper tape has proved to be an effective protective
measure for the prevention of tarnish and the
preservation of daguerreotypes. To date, there is no
remedy for damage caused by glass deterioration.
Cleaning and reusing the old cover glasses will not
remedy the problem, and, in fact, will eventually make
it worse. Replacing the nineteenth century glasses
with modern, high-durability window glass will arrest
the problem. Daguerreotypes are relatively stable when
compared with other photographic materials, especially
if they are maintained in a controlled environment
(low relative humidity and moderate temperature) and
are well sealed.

ACKNOWLEDGMENT

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RAISING OF THE BOOK-PAPER LONGEVITY BY MEANS OF CHELATES AND CA-CHELATE COMPOUND

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SUMMARY

Any type of paper contains ions of heavy metals. Being the catalysts of the oxidizing destruction of cellulose, they decrease paper longevity.
The possibility of paper stabilization as a result of treatment with chelates (OEDF and DTPA) and Ca-chelate compound was investigated. The effect of paper stabilization was achieved by removing of ferric and cupric ions and simultaneous introducing of calcium ions, the latter being a product of Ca-chelate compound dissociation.
Mechanical strength, brightness degree, pH of cold extraction of the paper treated as well as untreated were taken as a function of time of artifical ageing. The evaluation of stabilizing effect of chelates and Cachelate compound on paper was made by using the kinetic concept of strength and thermogravimetric analysis.

The Ca and Mg bicarbonates solution, suggested by an American investigator Barrow, is successfully used to neutralize the acid pro - ducts of cellulose degradation as a result of paper storage and subsequently to stabilize the paper / 1 /. The effectiveness of the treatment decreases, however, it the paper contains transition metals such as Fe, Cu, Co, which accelerate oxidization processes resulting into degradation of cellulose and paper when moistured. This type of degradation doesn't appear when the "dry" method of accelerated ageing is used. The investiga - tions showed that even paper having a gua - ranteed alkaline reserve but containing oxi- dizing metal - catalysts fail to be suffici- ently durable / 2 /.
Metal traces in paper occur due to its manu- facturing technology. The catalysts are in- troduced into paper from wood, boiling acid, grinders, metal casting net and water.

The quantitative content of Fe^{3+} and Cu^{2+} ions in industrial paper is ascertained ex- perimentally by means of o-phenantroline (Fe^{3+}) and cuprison (Cu^{2+}). The results are presented in Table 1.
The object of the work was to develop an ef- fective method of extracting ions of heavy metals from paper and, thereby, increase its stability.
The compounds found to be sufficiently effec-
tive for inactivation of Fe^{3+} and Cu^{2+} ions are complex compounds-chelates, which bind ions of heavy metals in water. Chelates are organic compounds able to coordinate cation with two or more donor atoms. They consist of chalate ligands - acid and alkali center com- bined. A number of chelates were investigated and diethylenethreeaminpentaacetate (DTPA) and oxyethylenediphosphonic (OEDP) appeared to be the most effective.

Table 1

Percentage of transitional metal ions in paper

Type of paper	Ions content, %	
	Fe^{3+}	Cu^{2+}
Newsprint	0.0057	0.0027
Offset	0.0169	0.0016
100% sulphite cellulose	0.0056	0.0005

Experimental paper sumples were treated with chelates. The type of chelate, its concentra- tion, temperature, pH duration of the treat- ment and of the subsequent washing varied. The experiments carried out resulted in deve- loping optimal conditions of paper treatment by DTPA and OEDP for extracting Fe^{3+} ions from paper. The conditions are as follows: concentration of the solution 2%, duration of treatment 1 h, T 60°C, pH 5,4 and duration of washing 30 min. Optimal conditions and the type of chelate for Cu^{2+} ions extraction, are the same with the exception of pH which should be 6.5. The simultaneous extraction of Fe^{3+} and Cu^{2+} ions is optimal when pH is kept at the rate of 6.0 with the help of am- monia solution. Table 2 presents the quantity of Fe^{3+} and Cu^{2+} ions extracted.

Table 2

Fe^{3+} and Cu^{2+} amount extracted from paper by means of DTPA solution for various pH

Type of paper	pH value		
	3.4	5.4	6.5
Fe^{3+} extracted, %			
Newsprint	61.0	74.0	37.0
Offset	10.0	17.0	16.0
100% sulphite cellulose	34.0	59.0	58.0
Cu^{2+} extracted, %			
Newsprint	87.0	91.0	93.0
Offset	75.0	77.0	86.0
100% sulphite cellulose	64.0	76.0	84.0

It should be noted that the amount of Cu^{2+} ions extracted is more than that of Fe^{3+} ions in all cases, while the highest results are obtained with newsprint.
The effect of the stabilization of chelates on paper was estimated. The types of paper used in the experiment were treated with DTPA solution in accordance with the above - menti- oned conditions and together with the control untreated samples were subjected to accele- rated ageing to estimate the rate of change of paper proporties during storage.
Accelerated ageing was carried out in tightly closed glass tubes in thermostat under natu- ral air circulation and T 105 ± 2°C for 3, 6, 9 and 12 days. The samples were then tested for folding endurance and pH of the paper wa- ter extract was determined. The results are presented at Fig. 1, 2.
Thus, chelate treatment leads to a decrease of the paper degradation rate and riseing its stability for all 3 types of paper under in- vestigation. One should point out, however, that chelate treatment results in some increa- se of the investigated values initially.
To estimate the change of paper brightness the sumples were prepared on the leaf-casting apparatus.
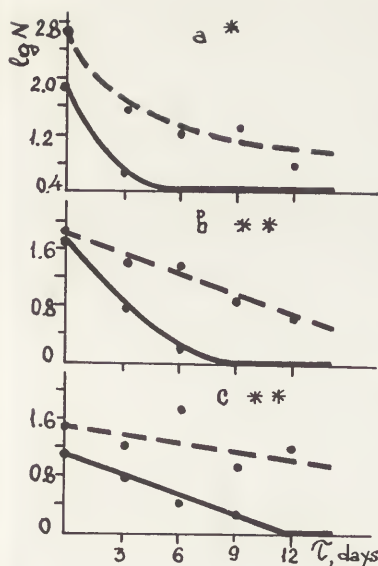
Fig. 1.
Logarythm of the number of double folds (lg N) vs. time of accelerated ageing (τ).
 a – newsprint
 b – offset paper
 c – 100% cellulose paper
------ untreated
- - - treated with DTPA solution
* measurement made under load 3.9 N
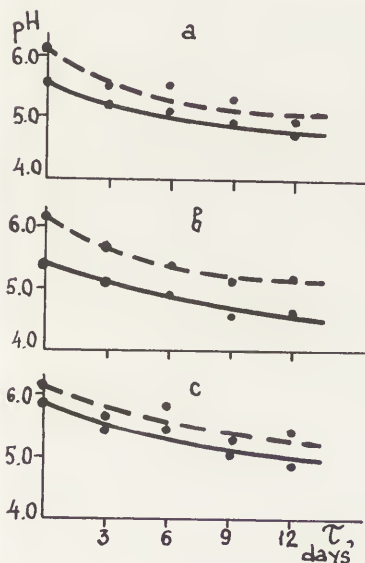** measurement made unter load 6.9 N

Fig. 2.
Paper water extract pH vs. time of accelerated ageing (τ)
For designations see Fig. 1.

The salts $Fe_2(SO_4)_3$ and $CuSO_4$ were introduced into the paper pulp for a part of the samples. Some of the samples were produced using distilled water to minimize heave metal ions content in paper. The results of measurement of brightness carried out with the Leikometr with a blue filter are presented in Fig. 3. The date obtained show that the brightness and stability increase as the heavy metal ions content in the paper decreases.
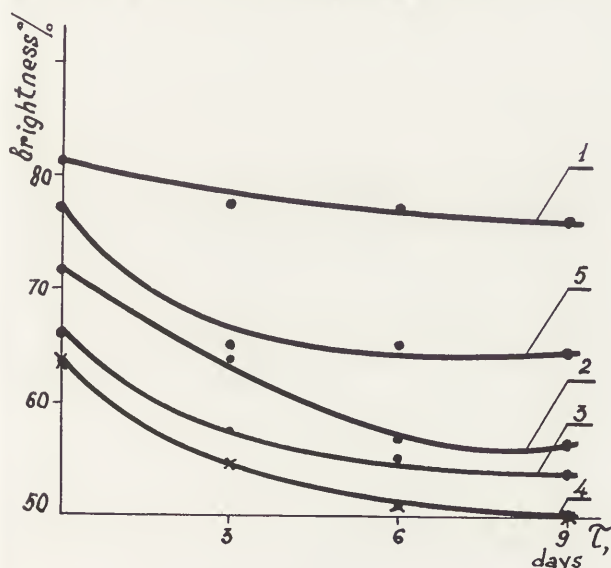

Fig. 3. Brightness of 100% sulphite cellulose paper vs. time of accelerated ageing (τ) for various contents of heave ions.
Paper pulp made in:
1) distilled water (C_{Fe}= 0.0038%),
2) plumbing water (C_{Fe} = 0.0158%), C_{Cu} = = 0.0023%),
3) plumbing water with addition of $Fe_2(SO_4)_3$ solution (C_{Fe} = 0.0176%),
4) plumbing water with addition of $CuSO_4$ (C_{Cu} = 0.0098%),
5) paper from paper pulp as in 2), treated with DTPA solution (C_{Fe} = 0.0087%, C_{Cu} = 0.0017%).

Extracting these metal ions by means of DTPA ensures stability of brightness. Nevertheless values of brightness are higher for paper produced in distilled water.
Subsequently the consecutive effect of DTPA and Ca and Mg bicarbonates on paper was studied. With that end in view paper samples were treated for 1 hour with 2% solution of DTPA under the above-mentioned conditions. After washing these in distilled water, they were immersed for 1 h in Ca and Mg bicarbonates solution, concentration $6.5 \cdot 10^{-3}$ gm eqv/litra and pH 7.25. After 24 hours drying in the air the samples were subjected to accelerated ageing under the above-mentioned conditions. The results of determination of the folding endurance values and pH of the newsprint water extract are presented at Fig. 4.
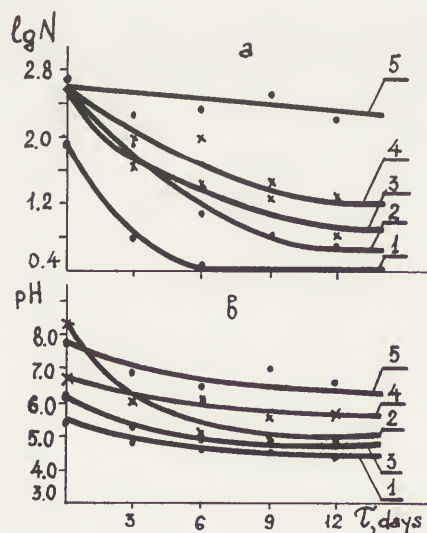
Fig. 4.
Changes in the properties of newsprint subjected to various types of stabilization processes vs. time of accelerated ageing (τ)
a) Logarythm of the number of double folds (lg N)
b) Water extract pH.

1. Untreated paper.
2. Paper treated with Ca and Mg bicarbonates.
3. DTPA solution treatment.
4. Ca – DTPA treatment.
5. DTPA + Ca and Mg bicarbonate treatment.

The results prove that the paper stability after consecutive treatments with DTPA solution and Ca and Mg bicarbonates solution is significantly higher then that of the papers treated separately. These results are well confirmed (Table 3) by the calculations of the activation energy for paper deterioration according to the procedure based on the kinetic concept of strength (Uo) 3 and thermogravimetric analysis (E).
In the next stage of the work the possibility of using metal – chelate compounds to stabilize the paper was studied. Those considered were DTPA + alkali – earth metals and particulary Ca-DTPA.
Logarythm of the constant of stability of Ca – DTPA

Ca − DTPA (lg K_{St} = 10.89) is reported [4]
to be significantly lower that of Cu − DTPA
(lg K_{St} = 21.5) and Fe − DTPA (lg K_{St} = 22.5)
pH 6. On the basis of these date it was
suggested that, provided pH is 6, the pro-
duct of dissociation, i. e. chelate would
extract from paper and bind tightly heavy
metal ions, while Ca^{2+} ions would react wit
with carboxy groups of cellulose promoting
its stabilization.
The experiment was carried out with the same
types of paper as with the previous compo-
unds. The stability effect was evaluated ac-
cording to the results of accelerated ageing
under the above-mentioned conditions on the
basis of changes in folding endurance value,
water extract pH, brightness and in compari-
son with the effect of Ca and Mg bicarnona-
tes on paper. The results of the experiments
are presented in Table 3 and Fig. 4 (Cuvre
4). The analysis of the results shows that
newsprint treated with Ca − DTPA has a slower
rate of Change in properties under ageing as
compored to that of the control samples and
that of the samples treated with Ca and Mg
bicarbonates solution. At the same time, the
stability effect of DTPA + Ca and Mg bicar-
bonates on paper appears to be the highest.

Table 3.

Values of activation energy for deterioration
of newsprint subjected to various types of
stabilization

Type of treatment	Activation energy (Uo), kJ/mol	Activation energy (E), kJ/mol
Untreated	126.50	124.40
DTPA	127.70	124.70
Barrow buffer	128.30	125.40
DTPA + Barrow buffer	131.20	129.10
Ca − DTPA	129.00	126.20

Analysis of this phenomenon and a search for
ways to get higher results is the object of
further investigations.
Thus, a number of experiment on paper treat-
ment with chelates and Ca − DTPA aiming at
its stabilization prove the work in this
field to be very promissing.

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ETUDE EXPERIMENTALE DE LA DETERIORATION ET DE LA RESTAURATION CHIMIQUE DES EPREUVES PHOTOGRAPHIQUES SUR PAPIER SALE

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RESUME

Très tôt dans l'histoire des techniques photographiques l'altération des épreuves sur papier salé a posé un problème majeur. C'est la raison pour laquelle nous avons étudié expérimentalement ce procédé. Dans ce but, des échantillons de papiers salés ont été vieillis artificiellement dans diverses atmosphères. On a pu ainsi comparer les effets de la chaleur humide, des gaz polluants (dioxyde d'azote, anhydride sulfureux, acide sulfhydrique), du peroxyde d'hydrogène et de la lumière sur quatre procédés de papiers salés, réalisés sur deux papiers de support différents.
Des traitements chimiques ont enfin été appliqués aux images altérées afin de tenter d'en retrouver les caractères originaux. Trois traitements ont été retenus pour leurs bons résultats visuels. Nous avons donc analysé leur comportement vis-à-vis des supports. Il convient néanmoins de considérer ces résultats comme une première approche, encore expérimentale, du problème.

Les techniques de tirage sur papier salé ont une place privilégiée dans les collections photographiques du 19e siècle. D'une très grande qualité esthétique, ce procédé a été largement utilisé en France des années 1840 à 1860 environ, et s'inscrit donc dans une période importante pour l'histoire de la photographie. Ces images sont obtenues par noircissement direct, sur une feuille de papier sensibilisée à la lumière par du chlorure d'argent. Comme la majorité des procédés à noircissement direct, elles sont particulièrement sensibles aux agents de détérioration et prennent souvent une coloration jaunâtre dans le temps qui peut, dans les cas extrêmes, ne laisser sur la feuille qu'une image fantôme à peine identifiable. Nous avons essayé d'analyser les divers mécanismes d'altération des épreuves afin de pouvoir, dans un deuxième temps, nous pencher sur les problèmes de la restauration chimique des images pâlies.

1. La fabrication des échantillons

L'analyse de quelques épreuves anciennes nous a permis de déterminer la composition fibreuse et la nature de l'encollage des papiers de support, afin de confirmer certaines données fournies par la littérature photographique de l'époque. Deux groupes distincts se sont dessinés. D'un côté, les épreuves d'origine française (E. Baldus, A. Poitevin et anonymes) sont obtenues sur un papier de support composé de pâte de lin et de bourre de coton. Leur encollage est à base d'amidon et de colophane. L'autre groupe de papiers est composé par les épreuves fabriquées en Angleterre, par W.H. Fox Talbot, à base de fibres de coton et encollées à coeur par de la gélatine. En nous basant sur ces résultats, nous avons retenu deux types de papier de support correspondant à ces deux groupes, afin de contrôler leur influence sur le comportement des images :

- un papier Arches Aquarelle satiné, dont la pâte est en linters de coton, encollé à coeur par de la gélatine

- un papier Renage, également en linters de coton, mais encollé par de l'amidon et de la colophane.

A partir de ces supports, nous avons sélectionné parmi les nombreuses techniques de papiers salés quatre variantes de fabrication : (voir annexe 1)

- *Les papiers salés simples* : il s'agit du premier procédé historique tel qu'il fut inventé par W.H. Fox Talbot. Les feuilles sont imprégnées d'une solution de chlorure de sodium ("salage"), mises à sécher, puis sensibilisées avant usage par une solution de nitrate d'argent. L'image se forme alors directement sous le négatif par exposition à la lumière. Elle est fixée, après un court rinçage, dans un bain de thiosulfate de sodium, puis lavée à l'eau courante.

- *Les papiers salés au bichromate de potassium* : surtout employé au tournant du siècle, ce procédé plus tardif et plus rare procure une image au meilleur contraste, grâce à l'adjonction de bichromate de potassium dans le bain de salage. De l'acide nitrique est ajouté au bain d'argent pour augmenter la sensibilité des feuilles. Les épreuves sont enfin mieux fixées et mieux lavées.

- *Les papiers salés avec un encollage additionnel et virés à l'or* : l'encollage additionnel au bain de salage est composé d'amidon (papiers salés à l'amidon) ou de gélatine (papiers salés à la gélatine). Après l'exposition, les épreuves sont virées à l'or avant d'être fixées. Ces deux procédés deviennent fréquents à partir des années 1850.

2. Méthodes d'analyse des épreuves expérimentales

L'évolution des échantillons est contrôlée par des méthodes optiques et chimiques. On mesure la densité optique sur les hautes, moyennes et basses densités d'une gamme de gris incluse dans l'image, avec un densitomètre MACBETH TR 524. Les résultats des variations de densité sont enregistrés et reproduits sur des histogrammes. D'autre part, le dosage des sels résiduels au traitement de fabrication permet de contrôler leur influence sur l'instabilité des images lors du vieillissement artificiel. Les dosages de thiosulfate résiduel ont été obtenus par la méthode photométrique au bleu de méthylène selon la norme ANSI PH4-8 (2). La présence de composés argentiques résiduels a par ailleurs été testée selon la norme ISO R 421 (1965). Enfin, un contrôle de l'évolution de l'acidité des échantillons au cours des différentes phases expérimentales a été effectué. Afin de vérifier l'innocuité des traitements vis-à-vis des supports, l'analyse de la résistance physico-chimique des papiers a été réalisée, selon les normes AFNOR, avant et après traitement, ainsi qu'après un cycle de vieillissement artificiel (7 jours à 87° et 60 % H.R.).

3. Etude de la dégradation des papiers salés

Celle-ci a été menée par vieillissement accéléré dans les atmosphères suivantes :

La chaleur humide : les échantillons ont été maintenus pendant une période de 2 à 23 jours à 60 % d'humidité relative et 90°C. Un jaunissement des zones de basses densités intervient dès le second jour, puis se stabilise. Il est accompagné d'une perte du contraste général de l'image (baisse des moyennes densités). Cette altération des demi-teintes est toujours plus brutale dans le cas des papiers salés simples dont le taux de thiosulfate résiduel est le plus élevé : 4 μg/cm2 pour 0,2 à 0,3 μg/cm2 en moyenne dans les autres cas. La norme ANSI PH4-8 donne la limite maximale de 0,7 μg/cm2 de thiosulfate résiduel pour une bonne conservation des épreuves (2). On observe des différences importantes de comportement selon la nature des papiers de support et celle du procédé de fabrication des épreuves. Les papiers encollés à coeur à la gélatine ont toujours un taux de jaunissement plus élevé que ceux qui ont été encollés à la résine et à l'amidon. Les papiers salés bichromatés sont par ailleurs les seuls à être peu touchés par la chaleur humide (1,3 % à 6 % de perte dans les hautes densités après 23 jours de vieillissement contre 10 % à 11 % dans le cas des autres procédés). Le faible taux de thiosulfate résiduel ainsi que la présence du bichromate, jouent ici sans doute un rôle protecteur.

On a, d'autre part, étudié l'effet de la température dans des conditions hygrométriques très élevées (95 % H.R.). Il est apparu qu'une chaleur élevée (90°C) procure une intensification importante des basses densités ainsi que des papiers de support. Ce phénomène ne se reproduit pas à une température plus modérée (30°C) comme le montre le tableau ci-dessous.

T A B L E A U   1

VARIATION DES 8ASSES DENSITES DE L'IMAGE APRES 15 JOURS A 95 % H.R.

(papier de support : Arches)

Procédés	Papier salé simple			Papier salé gélatiné viré à l'or		
Filtres	bleu	vert	rouge	bleu	vert	rouge
température : 90°C	+ 0,21	+ 0,15	+ 0,06	+ 0,41	+ 0,30	+ 0,20
: 30°C	- 0,01	- 0,02	- 0,04	- 0,01	0	- 0,03

La pollution : les effets de l'anhydride sulfureux à une concentration de 25 ppm et de 10 ppm de dioxyde d'azote en atmosphère humide (90 % H.R, 30°C) ont été analysés.

L'anhydride sulfureux seul ne possède qu'un effet lent sur les images. Une chute des densités moyennes, correspondant à un pâlissement, apparaît vers le douzième jour de vieillissement. Au bout de 18 jours, la perte d'information visuelle est pourtant importante et l'on enregistre une chute prononcée des hautes et surtout des moyennes densités (tableau 2). On a, d'autre part, remarqué que les images des papiers salés simples, sans encollage ni virage protecteurs, sont attaqués plus rapidement que les autres, mais perdent moins de densité moyenne en fin de vieillissement. Ce phénomène s'explique sans doute par une sulfuration plus poussée de l'argent comme l'indique la coloration verdâtre prise par les épreuves. Le sulfure d'argent très stable ne semble plus touché par une action prolongée du gaz polluant. Par contre, dans les zones de forte densité, qui possèdent beaucoup d'argent métallique, les papiers salés simples enregistrent une perte de densité plus forte que celle des autres procédés. Tout se passe ici comme si le phénomène était retardé. Il faut enfin noter que les papiers salés simples possèdent au départ un contraste beaucoup plus faible que les autres.

T A B L E A U   2

PERTE DE DENSITE APRES 18 JOURS DE 25 ppm DE SO$_2$, H.R. = 90 %

(papier support : Arches)

Procédés	Papier salé simple	Papier salé bichromaté	Papier salé gélatiné viré à l'or	Papier salé à l'amidon viré à l'or
Moyennes densités	50 %	85 %	82 %	72 %
Hautes densités	64 %	20 %	32 %	15 %

Le dioxyde d'azote produit, par contre, dans les mêmes conditions, une action très rapide sur l'image. La dégradation la plus brutale s'opère du premier au cinquième jour de vieillissement. Après cette période, elle est ralentie mais a déjà atteint un taux presque maximal pour tous les procédés étudiés. Il faut, d'autre part, noter que le virage à l'or se montre ici insuffisant pour protéger l'image (voir tableau 3).

Le mélange d'anhydride sulfureux et de dioxyde d'azote : si ce mélange procure par certains aspects une combinaison des deux formes d'altération, il faut en souligner les particularités : cette forme d'altération est plus poussé que celle obtenue par l'anhydride sulfureux seul, mais s'est montrée par contre moins brutale que lors des essais au dioxyde d'azote seul. Les demi-tons de l'image étant les premiers attaqués, ce phénomène est surtout visible dans les hautes densités(tableau 4).

T A B L E A U   3

PERTE DE DENSITE APRES 18 JOURS DE 10 ppm DE NO$_2$, H.R. = 90 %

(papier support : Arches)

Procédés	Papier salé simple	Papier salé bichromaté	Papier salé gélatiné viré à l'or	Papier salé à l'amidon viré à l'or
Moyennes densités	56 %	95 %	91 %	89 %
Hautes densités	55 %	51 %	58 %	51 %

T A 8 L E A U   4

PERTE DE DENSITE APRES UN VIEILLISSEMENT DE 18 JOURS DE 10 ppm DE NO$_2$ et 25 ppm DE SO$_2$, H.R. = 90 %

(papier support : Arches)

Procédés	Papier salé simple	Papier salé bichromaté	Papier salé gélatiné viré à l'or	Papier salé à l'amidon viré à l'or
Moyennes densités	57 %	90 %	87 %	87 %
Hautes densités	67 %	37 %	44 %	25 %

Cela s'explique sans doute par le fait que l'acide sulfurique ne peut que dans des conditions extrêmes former du sulfure ou du sulfate d'argent alors que l'acide nitrique (produit de décomposition du dioxyde d'azote) attaque rapidement l'argent en présence d'air humide. Dans le mélange des deux gaz, on obtient moins d'acide nitrique libre, celui-ci étant combiné en composés divers, tel que le sulfate acide de nitrosyle (voir C. CHAHINE et M. LEROY (4)). Ce phénomène réduit donc la corrosion de l'argent. Là encore, la plus forte altération des demi-teintes s'explique probablement par le taux moins élevé d'argent métallique qui s'y trouve.

L'acide sulfhydrique (H$_2$S) : l'action de l'acide sulfhydrique s'est montré trop rapide pour effectuer une étude évolutive.
Employé à une concentration de 0,2 %, une décoloration jaune verte de l'image intervient dès le deuxième jour dans le cas des épreuves non virées à l'or. Il s'agit là du mode de dégradation visuelle de l'image la plus poussée. Les épreuves virées à l'or, plus denses à l'origine, enregistrent également une perte importante de densité. Mais celle-ci s'assimile plutôt à un virage de teinte vers le gris brun et gêne moins la vision de l'image.

Le peroxyde d'hydrogène : les échantillons ont été soumis aux vapeurs de 30 % de peroxyde d'hydrogène à 110 volumes et 85 % d'humidité relative, pendant une période allant de 1 à 4 jours. Il se produit une décoloration ponctuelle des zones de hautes densités. Des piqûres rousses apparaissent sur les parties de l'image qui possèdent le plus d'argent métallique, alors qu'un blanchiment s'opère dans les demi-teintes. Si ce blanchiment est très réduit dans le cas des papiers salés virés à l'or, les taches rousses s'y développent par contre de manière privilégiée. Les papiers salés à la gélatine sont d'autre part plus touchés que ceux à l'amidon. Il faut néanmoins noter que, si cette forme d'altération a l'avantage de fournir une forme d'oxydation bien particulière, souvent décrite pour des matériaux photographiques modernes, elle est rare dans les collections de papiers salés anciens.

La lumière : l'exposition des échantillons a été effectué sous une lampe à vapeur de mercure de 400 watts (longueur d'onde de 280 à 760 nm) pendant une période de 2 à 90 jours. Ce mode de vieillissement se traduit, au bout du 45e jour par une légère intensification des blancs et une perte sensible des moyennes et hautes densités de l'image. Cette perte de densité s'accompagne d'un changement dans la teinte des épreuves qui tirent

vers le roux. Visuellement, la lumière agit donc sur les images à la manière d'un virage.

4. La restauration chimique des images

Les échantillons de papiers salés vieillis artificiellement ont servi pour examiner les traitements chimiques de restauration des images pâlies. La plupart des méthodes décrites dans la littérature ont été élaborées pour traiter les négatifs modernes. Il a donc été nécessaire de les adapter en fonction des caractéristiques particulières des papiers salés. Sept grandes classes de traitement ont été examinées :

Les virages à l'or : il s'agit des premiers traitements historiques de "revivification" des images (9). Plusieurs variantes ont été essayées, regroupées en bains acides, neutres et alcalins. Ceux-ci sont composés par une solution de chlorure double d'or et de sodium ou de potassium à laquelle on ajoute de l'acide acétique dans le premier cas, ou du bicarbonate de sodium dans les deux derniers. Les bains acides ont été abandonnés car ils attaquent les demi-tons de l'image. Les formules à base de chlorure d'or et de potassium à une concentration de 0,5 % se sont montrées les plus satisfaisantes, surtout appliquées à des épreuves déjà virées à l'or pendant leur fabrication. Mais si le contraste de l'image est bien amélioré, celle-ci prend une teinte bleutée qui rend ce traitement inapplicable aux papiers salés.

La réduction chimique des taches argentiques : on a essayé de réduire l'intensité des taches ponctuelles d'oxydation produites par le peroxyde d'hydrogène. L'emploi d'une solution d'iode pour réduire proportionnellement les sels d'argent (23) est inadéquate dans le cas des papiers salés. L'absence d'émulsion empêche de contrôler l'action de l'iode et la réduction de l'image argentique elle-même est plus rapide que celle des taches argentiques de surface. Les échantillons virés à l'or résistent mieux à ce traitement, sans doute grâce à leur meilleur contraste d'origine. La présence d'un encollage additionnel ralentit également la détérioration de l'image. Il en est de même dans le cas d'un traitement des taches par immersion dans un révélateur alcalin. Les taches rousses des épreuves virées au préalable s'atténuent sans pourtant disparaître.

Les traitements au chlorure mercurique : on a tenté d'obtenir une réduction partielle du jaunissement des épreuves à l'aide d'un bain de blanchiment au chlorure mercurique suivi d'une intensification de l'image dans une solution de chlorure de potassium ou de chlorure d'or et de potassium. Ces deux traitements ont été rejetés car, s'ils fournissent de très bons résultats dans le cas des épreuves virées à l'or, ils détruisent les images des papiers salés non virés. Plusieurs formules comprenant un blanchiment à base de chlorure mercurique et de bromure de potassium, suivi de divers modes d'intensification ont été essayées. Seul, le bain de noircissement composé par un révélateur alcalin (Kodak D-72) (21) a donné de bons résultats. Les épreuves s'intensifient de manière homogène et le contraste est nettement amélioré. La coloration verdâtre disparaît même dans le cas des papiers salés non virés à l'or, pour laisser la place à une teinte brun chaud (méthode 1, annexe 2).

Les intensifications aux sels de chrome : ces traitements consistent à blanchir les épreuves dans un premier temps par une solution à base de bichromate de potassium ou d'ammonium, puis à les développer dans divers révélateurs afin de retrouver l'image argentique qui peut être virée en dernier lieu. Bien que certaines de ces méthodes soient parfois citées dans la littérature comme étant applicables aux images à noircissement direct, toutes les variantes essayées ont été abandonnées en fonction du peu d'intensification qu'elles ont procuré aux papiers salés très dégradés.

Les traitements aux sels de cuivre : Les bains de blanchiment sont ici à base de chlorure cuivrique ou de sulfate de cuivre et de bromure de potassium. Là encore, aucune amélioration de l'image n'a été constatée celle-ci réapparaît dans le bain de noircissement trop pâle et sans contraste.

Les méthodes d'intensification argentique : leur mécanisme consiste à déposer de l'argent métallique sur l'image par l'intermédiaire d'un bain comprenant du nitrate d'argent soluble et un agent réducteur (21). Ces traitements ont donné des résultats médiocres (apparition de taches et piqûres brunes, coloration des blancs de l'image ...) lorsqu'elles sont appliquées telles quelles. Divers pré-traitements ont été effectués afin d'atténuer ces défauts (refixage préalable, utilisation d'un éliminateur d'hyposulfite, bain de neutralisation au métaborate de sodium ou diverses méthodes de réduction du jaunissement des épreuves. L'application de ces traitements préalables à l'intensification ont fourni des résultats médiocres, sauf dans le cas des épreuves virées à l'or ou peu dégradées. Une amélioration notable des résultats a pourtant été obtenue en traitant les papiers de supports par une solution de neutralisation au métaborate de sodium et un blanchiment à l'hypochlorite de calcium suivi d'un bain de sulfoxylate formaldéhyde de sodium. Grâce à ce blanchiment préalable, les blancs restent purs en fin de traitement et l'intensification s'effectue de manière homogène, même dans le cas des papiers salés simples très altérés. Les épreuves prennent une teinte brune qui se rapproche de leur tonalité originale (méthode 2, annexe 3).

Les blanchiments de l'image au permanganate de potassium
Les formules à base de blanchiment au permanganate de potassium appliquées sans modification (21) ont également fourni de mauvais résultats sur les papiers salés. Les images deviennent grises et trop pâles à la suite du développement. Plusieurs essais ont été tentés avec différents temps de blanchiment et plusieurs révélateurs, afin de produire des tons plus chauds. Les résultats sont dans l'ensemble médiocres. Par contre, lorsque ce traitement est suivi d'une intensification argentique, on obtient d'excellents résultats visuels dans le cas des papiers salés bichromatés, même très dégradés (méthode 3, annexe 4). Les papiers salés simples restent là encore plus difficiles à restaurer.

Résistance physico-chimique des papiers traités :

On a analysé la résistance des papiers de support après traitement par les trois méthodes de restauration qui se sont montrées les plus satisfaisantes. La meilleure résistance des supports est obtenue avec le traitement d'intensification argentique précédé d'un bain d'hypochlorite de calcium. Les papiers Arches Aquarelle et Renage semblent tous deux protégés par le traitement, comme le montre leur bonne tenue au vieillissement accéléré. La méthode à base de chlorure mercurique et d'un développement alcalin procure par contre une baisse trop importante de la résistance des deux papiers de support après le vieillissement artificiel. Enfin, les résultats les plus mauvais ont été obtenus par le blanchiment au permanganate de potassium, suivi de l'intensification argentique. C'est ici le papier de Renage qui a, en général, moins bien résisté au traitement. Il faut enfin noter que la présence d'un taux élevé de gélatine dans les papiers Arches a rendu difficile la mesure de l'indice de cuivre et du degré de polymérisation viscosimétrique (annexes 5, 6, 7).

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Ainsi, il semble bien que le comportement des échantillons aux différents traitements de restauration confirme les observations faites lors de l'étude de leur dégradation : chaque groupe de papier salé réagit différemment à un même traitement ; les papiers salés sans encollage additionnel et non virés à l'or sont plus altérés par les agents chimiques et leur image est plus difficile à restaurer. La nature du papier de support intervient également sur le comportement des images : les épreuves fabriquées sur Arches satiné ont mieux résisté à la dégradation et sont donc plus faciles à restaurer. Malgré les nombreuses difficultés que nous avons rencontrées lors des traitements, il a néanmoins été possible d'obtenir des améliorations réelles de la qualité visuelle

des images très altérées. Cependant tout traitement chimique doit être appliqué avec une très grande prudence. En effet, lors des différentes phases de cette étude, on a pu constater que les papiers salés forment un groupe technologiquement très peu homogène et complexe dont chaque variété possède des réactions particulières. Ainsi, avant toute intervention chimique sur une épreuve il paraît indispensable de pouvoir identifier la nature exacte du procédé dont il s'agit et de s'appuyer sur des méthodes permettant un meilleur contraste original des images. Il faut, enfin, en fonction du caractère d'irréversibilité de ces traitements, considérer ces résultats comme une première approche expérimentale dont le but est de mieux comprendre le comportement et la spécificité sur papier salé.

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ANNEXES

A N N E X E   1

COMPOSITION DES BAINS UTILISES POUR LA FABRICATION DES ECHANTILLONS

Composition des bains	Papier salé simple	Papier salé bichromaté	Papier salé gélatiné viré à l'or	Papier salé à l'amidon viré à l'or
SALAGE				
eau distillée	1 l.	1 l.	900 ml	1 l.
alcool			100 ml	
chlorure de sodium	50 g.	18 g.		35 g.
chlorure d'ammonium		12 g.	20 g.	
bichromate de potassium		1 g.		
citrate de sodium			10 g.	
acide citrique				3 g.
gélatine			20 g.	
amidon de riz				35 g.
SENSIBILISATION				
eau distillée	1 l.	1 l.	1 l.	1 l.
nitrate d'argent	150 g.	140 g.	140 g.	140 g.
acide citrique		40 g.	40 g.	40 g.
acide nitrique (3 N)		10 ml	10 ml	10 ml
VIRAGE				
eau distillée			1 l.	1 l.
chlorure d'or à 1 %			21 ml	21 ml
carbonate de sodium			1 g.	1 g.
acétate de sodium			7 g.	7 g.
FIXAGE				
eau distillée	1 l.	1 l.	1 l.	1 l.
thiosulfate de sodium	150 g.	250 g.	150 g.	150 g.
sulfite de sodium		20 g.		
PRE-LAVAGE				
eau distillée		1 l.		
sulfite de sodium		10 g.		
LAVAGE				
eau courante	1 h.30	1 h.	1 h.30	1 h.30

ANNEXE 2

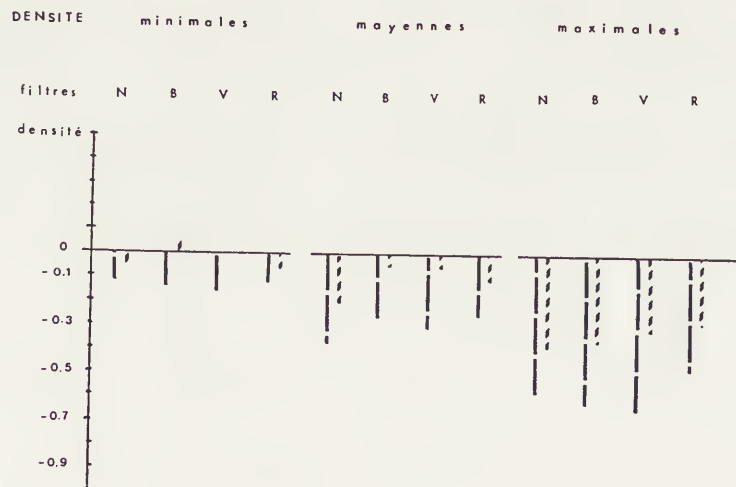
VARIATION DENSITOMETRIQUE D'UN PAPIER SALE SIMPLE,
vieilli à l'acide sulfhydrique, puis traité par la méthode 1 (chlorure mercurique)
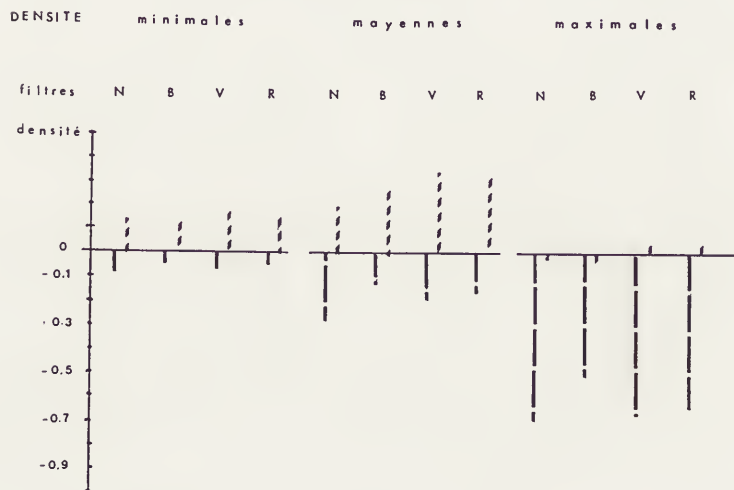

ANNEXE 3

VARIATION DENSITOMETRIQUE D'UN PAPIER SALE SIMPLE,
vieilli à l'acide sulfhydrique, puis traité par la méthode 2 (intensification argentique)

ANNEXE 4

VARIATION DENSITOMETRIQUE D'UN PAPIER SALE SIMPLE,
vieilli à l'acide sulfhydrique, puis traité par la méthode 3 (blanchiment
au permanganate de potassium)

filtres N: visuel
        B: bleu   _____ après dégradation
        V: vert   - - - - - - après restauration
        R: rouge

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ANNEXE 5 : ANALYSES PHYSICO-CHIMIQUES DE LA RESISTANCE DES PAPIERS TRAITES PAR LA METHODE 1 (chlorure mercurique)

	Longueur de rupture en m.			Allongement			Résistance éclatement		Résistance au déchirement			Degré de polymérisation viscosimétrique		Indice de cuivre		pH
	ST	SM	Var.%	ST	SM	Var. %		Var. %	ST.	SM	Var. %		Var. %		Var. %	
Arches témoin 3 h. dans l'eau	2905	5025		5,11	3,75		2,27		904	756				0,71		6,60
Arches traité	2670	4775	- 6,5	5,06	4,31	+ 7	2,54	+ 11,9	855	671	- 8,3			0,55	+ 22	8,15
Arches témoin vieilli 3 h. dans l'eau	2450	4290		4,03	3,39		2,1		770	636				1,22		6,60
Arches traité vieilli	2287	4122	- 5,3	2,6	2,3	- 34	1,78	- 15,2	699	509	-14,6			0,70	+ 42	7,15
Renage témoin 3 h. dans l'eau	1655	2935		5,17	2,92		1,4		659	599		614		0,48		6,75
Renage traité	1550	2685	- 7,4	4,96	2,59	- 7,5	1,24	- 11,4	639	618	0	622	+ 1,3	0,39	+ 19	7,60
Renage témoin vieilli 3 h. dans l'eau	1520	2710		5,03	2,47		1,3		637	566		484		0,72		6,40
Renage traité vieilli	1531	2702	+ 0,5	3,96	1,87	-22,8	1,1	- 15,4	577	561	- 5,15	560	+ 15,7	0,46	+ 36	7,05

ANNEXE 6 : ANALYSES PHYSICO-CHIMIQUES DE LA RESISTANCE DES PAPIERS TRAITES PAR LA METHODE 2 (intensification argentique)

	Longueur de rupture (m.)			Allongement			Résistance éclatement		Résistance au déchirement			Degré de polymérisation viscosimétrique		Indice de cuivre		pH
	ST	SM	Var.%	ST	SM	Var.%		Var.%	ST	SM	Var.%		Var.%		Var.%	
Arches témoin 3 h. dans l'eau	2905	5023		5,11	3,75		2,27		904	756				0,71		6,60
Arches traité	2714	4670	- 6,8	4,82	3,86	- 1,4	2,5	10,13	904	699	- 3,75			0,85	-19,7	9,20
Arches témoin vieilli 3 h. dans l'eau	2449	4288		4,03	3,39		2,1		770	636				1,22		6,60
Arches traité vieilli	2773	4979	+14,65	3,53	2,92	-13,15	2,2	4,76	713	579	- 8,2			1,02	+16,4	8,60
Renage témoin 3 h. dans l'eau	1655	2937		5,17	2,92		1,4		659	599		614		0,48		6,75
Renage traité	1534	2653	- 8,5	4,66	2,7	- 8,7	1,3	-7,14	642	615	+ 0,1	589	- 4,1	0,46	+ 4,2	8,90
Renage témoin vieilli 3 h. dans l'eau	1519	2710		5,03	2,47		1,3		637	566		484		0,72		6,40
Renage traité vieilli	1436	2570	- 5,35	3,93	2,1	-18,5	1,3	0	610	615	+ 2,25	611	+26,2	0,55	+23,6	8,85

ANNEXE 7 : ANALYSES PHYSICO-CHIMIQUES DE LA RESISTANCE DES PAPIERS TRAITES PAR LA METHODE 3 (blanchiment au permanganate de potassium)

	Longueur de rupture (m.)			Allongement			Résistance éclatement		Résistance au déchirement			Degré de polymérisation viscosimétrique		Indice de cuivre		pH
	ST	SM	Var. %	ST	SM	Var. %		Var. %	ST	SM	Var. %		Var. %		Var. %	
Arches témoin 3 h. dans l'eau	2905	5023		5,11	3,75		2,27		904	756				0,71		6,60
Arches traité	2516	4479	-12,1	4,48	4,92	+21,5	2,3	+ 1,3	741	565	-21,6			1,32	- 86	8,05
Arches témoin vieilli 3 h. dans l'eau	2449	4288		4,03	3,39		2,1		770	636				1,22		6,60
Arches traité vieilli	2474	4419	+ 2	3,27	2,55	-21,8	2	- 4,8	656	508	-17,4			1,18	+ 3,3	7,3
Renage témoin 3 h. dans l'eau	1655	2937		5,17	2,92		1,4		659	599		614		0,48		6,75
Renage traité	1455	2554	-12,5	3,66	2,13	-19,5	1,1	- 21	558	514	-14,7	404	-34,2	0,63	-31,2	7,5
Renage témoin vieilli 3 h. dans l'eau	1519	2710		5,03	2,47		1,3		637	566		484		0,72		6,4
Renage traité vieilli	1352	2380	-11,6	3,3	1,9	-28,7	0,95	- 26,9	539	500	-13,5	518	+ 7	0,66	+ 8,3	7,5

L'ASSECHEMENT DU CUIR PAR LYOPHILISATION

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RESUME

Au cours de la lyophilisation, le cuir peut subir une
rétraction d'autant plus importante qu'il est plus
dégradé. Afin d'établir la cause de ce phénomène,
différents facteurs ont été modifiés à chacune des
phases de la lyophilisation. Il a été établi que le
retrait du cuir est dû à un séchage trop poussé surve-
nant lors de la dessication secondaire.

Le cuir ainsi séché doit reprendre un taux normal
d'humidité, pour revenir à ses dimensions originales
et une réhydratation progressive facilite le phénomène.
Cependant, pour un cuir dégradé qui se remet plus dif-
ficilement en équilibre avec l'humidité relative envi-
ronnante, l'utilisation de cryoprotecteurs est une
solution pour pallier cet inconvénient.

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La lyophilisation est une méthode d'assèchement qui a
été utilisée avec succès dans de nombreux cas pour
traiter des documents inondés. Mais si elle ne pose
pas de problème pour les papiers (1), il n'en est pas
de même pour le cuir qui subit un rétrécissement di-
mensionnel pouvant atteindre 4 à 6 % pour le cuir neuf
et 10 % pour un cuir dégradé.

Ce travail a pour but de trouver les raisons de ce ré-
trécissement afin d'y remédier. Nous avons pu établir
que celui-ci est dû à un séchage trop poussé du cuir,
inhérent à la technique.

En effet, l'eau est un élément important que le cuir
doit contenir, en quantité suffisante pour rester
souple. Pour une température donnée, la teneur en eau
varie en fonction de l'humidité relative avec laquelle
il est en équilibre. On estime que dans l'idéal il
devrait en contenir 14 % et être conservé à 55 % H.R.
et 18°C.

Cette eau est retenue dans le cuir par des mécanismes
mettant en jeu des niveaux d'énergie différents, une
partie étant fixée par liaisons hydrogène aux groupe-
ments hydrophiles du collagène et constitue l'eau
"liée". L'assèchement devrait donc éliminer uniquement
l'eau d'imbibition, c'est-à-dire en excès, en conser-
vant au cuir une certaine teneur en humidité.

1. LA LYOPHILISATION

1.1. Principe

Rappelons brièvement que le phénomène peut se décompo-
ser en trois phases (4) :

1°/ congélation, transformation de l'eau libre en glace.
L'eau "liée" chimiquement à la protéine et l'eau se
trouvant "immobilisée" dans la structure du tissu ne
sont pas congelables.

2°/ Dessication primaire ou sublimation proprement dite.
La transformation de la glace en vapeur nécessite d'opé-
rer à basse pression et à basse température, elle se
fait à partir de la surface libre de l'échantillon, ce
qui laisse une couche superficielle sèche, le front de
sublimation se déplaçant ensuite en profondeur.

3°/ Dessication secondaire ou désorption ; il se pro-
duit une évaporation de l'eau "immobilisée" et une dé-
sorption de l'eau "liée" chimiquement.

Dans certains cas, la phase 3 peut commencer avant que
la phase 2 soit terminée. En effet, la couche sèche,
bien que traversée par le flux de vapeur provenant de
la couche encore congelée, peut subir une désorption
s'il existe un écart suffisant entre la pression de
vapeur de l'eau "liée" sur le produit et la pression
partielle de vapeur d'eau dans la chambre de dessication.

1.2. Appareillage

Nous avons utilisé un lyophilisateur USIFROID du type
SMH 15 dont la chambre de dessication a une capacité
de 75 litres. Celle-ci comprend une étagère (40x30 cm)
traversée par le fluide de refroidissement ou de ré-
chauffement, sur laquelle sont placés les échantillons.
Au-dessous de l'étagère est situé le condensateur qui
piège la vapeur d'eau au fur et à mesure de son extrac-
tion. L'appareil permet de travailler à une pression
minimum de 0,025 mmHg.

Toutes les expériences ont été réalisées sur des cuirs
de veau neuf et des fragments de reliures détériorées.

2. ETUDES DU MECANISME DE RETRECISSEMENT

Pour connaître à quelle phase de la lyophilisation sur-
vient le retrait, nous avons étudié successivement les
facteurs suivants :

2.2. Influence de la vitesse de congélation

Un refroidissement lent favorise la formation de gros
cristaux de glace irréguliers, alors que s'il est rapi-
de il donne naissance à des cristaux plus petits et plus
nombreux.

On pourrait s'attendre à ce qu'une modification de la
texture du tissu, qui devient plus grossière dans le
premier cas, ait une incidence sur le retrait. Nous
avons constaté qu'il n'en est rien.

Dans une première série d'essais, nous avons comparé
une congélation à -20°C dans un congélateur ménager
(refroidissement lent) à une congélation rapide dans
un appareil industriel, suivies d'une dessication à
-20°C. Dans une deuxième série, les cuirs ont été
congelés comme précédemment, puis la température a été
abaissée rapidement à -40°C avant la dessication
*quel que soit le mode de congélation, les cuirs rétrac-
tent de façon identique.*

2.2. Influence de la vitesse de sublimation

La sublimation est généralement plus rapide si la
substance a été refroidie lentement, l'extraction de
l'eau étant facilitée par une texture plus grossière.

D'autre part, la dessication étant un phénomène très
endothermique, pour qu'elle soit rapide, il faut que
la température au niveau du front de sublimation soit
le plus élevé possible tout en restant cependant in-
férieure à la température de fusion commençante du
système pour qu'il demeure congelé.

Les essais ont été effectués sur des cuirs congelés à
-20°C ou -40°C (congélation lente ou rapide). L'étagère
sur laquelle sont placés les échantillons a été réchauf-
fée en fixant sa température finale à +20°C, +10°C et
0°C avec des intensités de chauffage différentes.

*Tous les échantillons rétractent, quelle que soit la
vitesse de sublimation. Cependant, on observe une ré-
traction moins grande quand la température de l'étagère
est ramenée à la température la plus basse (0°C).*

2.3. Influence de la dessication secondaire

Nous pensons que dans le cas du cuir la désorption débute alors même que la sublimation de la glace n'est pas terminée et qu'elle est responsable du rétrécissement. En effet, nous avons constaté que si le vide est rompu au moment où la température d'un échantillon dépasse 0°C, ou celui-ci n'est pas encore sec, ou il a déjà rétracté, quellesque soient les conditions opératoires. En outre, le retrait est d'autant plus important que l'on prolonge la dessication secondaire et, comme nous l'avons vu précédemment, que la température maintenue au voisinage de l'échantillon est élevée. D'autre part, lorsque les cuirs sont sortis de l'appareil immédiatement après la rupture du vide, il se produit un échauffement sensible atteignant 30°C en quelques minutes. Ce phénomène, qui est dû à une adsorption brusque d'humidité par le cuir, nous amène à penser que le séchage a affecté l'eau liée.

Le comportement du cuir pendant le séchage a préoccupé de nombreux auteurs. HURLIMANN (3) mentionne des tests montrant que si l'humidité relative à laquelle il est conservé passe de 100 % à 0 %, un cuir de tannage végétal rétracte de 6 % et un cuir au chrome de 18 %. Selon Von FUCHS (2), si la concentration en eau descend au-dessous d'un certain seuil, les distances entre fibres de collagène approchent les dimensions moléculaires et des réticulations peuvent s'installer.

3 - LES REMEDES POSSIBLES

3.1. Importance de la réhydratation

Pour qu'un cuir "surséché" retrouve ses qualités mécaniques, il faut qu'il récupère une certaine teneur en eau, et la façon dont la réhydratation est conduite est capitale. En effet, nous avons pu constater dans nos expériences que des cuirs remis dans des conditions normales (autour de 50 % d'humidité relative) dès la rupture du vide accusent une rétraction importante. D'autre part leur taux d'humidité reste dans la plupart des cas inférieur de 1 % à celui des témoins non lyophilisés (cette perte d'eau n'est cependant pas proportionnelle au temps de la dessication secondaire comme peut l'être la rétraction).

Par contre, si l'on permet au cuir une réhydratation ménagée en le mettant dans une atmosphère où l'humidité relative est progressivement augmentée de 0 à 98 %, le cuir neuf ne subit aucune rétraction et le cuir dégradé une rétraction modérée. Grâce à la configuration de notre appareil où le condensateur est dans la chambre de dessication, il se produit une augmentation de l'humidité relative par évaporation de la glace (fixée sur le piège pendant la dessication) au fur et à mesure de l'élévation de la température ; on atteint ainsi 98 % H .R. en 3 à 4 heures. Nos échantillons ont été maintenus dans ces conditions une vingtaine d'heures ; puis, remis en atmosphère normale, ils ont nécessité encore une vingtaine d'heures pour que leur contenu en eau s'équilibre.

Des analyses effectuées sur des cuirs neufs de veau réhydratés selon ces deux techniques après lyophilisation, montrent des teneurs en humidité supérieures (de 1-1,2 %) pour les échantillons réhydratés de façon progressive.
Cependant, pour éviter toute rétraction du cuir dégradé, il serait intéressant d'expérimenter une réhydratation encore plus progressive, en prolongeant davantage le séjour à basse humidité relative pour laisser le temps à l'eau "liée" de reprendre sa place dans les structures affaiblies.

3.2. Utilisation de cryoprotecteurs

L'introduction de substances hygroscopiques dans le cuir est un palliatif pour retenir une certaine quantité d'eau au sein du matériau, et réduire ainsi l'importance de la désorption.

Différents glycols, à des concentrations de 10 à 50 % dans l'eau ont été expérimentés : propanediol 1-2, butanediol 1-3, butanediol 1-4, éthylèneglycol, diéthylèneglycol, triéthylèneglycol, polyéthylène glycol 400 et 600, ainsi que des polyalcools comme le glycérol et le sorbitol. Les cuirs mouillés ont séjourné 2 à 3 jours dans ces solutions avant d'être lyophilisés. Les échantillons ainsi traités, quel que soit leur état de dégradation, ne présentent aucun échauffement quand ils sont remis en atmosphère normale dès la rupture du vide. On a cependant intérêt à procéder à une réhydratation ménagée pendant quelques heures après la lyophilisation. Les concentrations optimales se situent entre 20 et 30 % : des concentrations inférieures n'offrent pas de protection suffisante contre la rétraction du cuir dégradé et des concentrations supérieures modifient trop l'aspect du matériau (couleur, toucher, souplesse).

Outre la protection contre la rétraction, le choix du glycol sera fait en fonction :

- de leur influence sur le comportement mécanique du cuir soumis à des variations hygrométriques ;

- de leur stabilité chimique au sein du cuir

- de la résistance fongique des cuirs imprégnés.

L'imprégnation d'un cuir de reliure présente un problème particulier dans la mesure où un livre, objet composite, ne peut être immergé dans une solution de glycol sans que l'on risque d'endommager les encres (ou le papier). Dans ce cas, le glycol devra être appliqué par badigeonnage ou pulvérisation.

CONCLUSION

La rétraction du cuir au cours de la lyophilisation étant due à un séchage trop poussé survenant lors de la dessication secondaire, celle-ci ne doit pas être prolongée inutilement. L'opération doit être arrêtée dès que la température des échantillons atteint des valeurs positives en maintenant l'étagère sur laquelle ils sont placés à une température peu élevée, proche de 0°C.
Le cuir doit reprendre une certaine quantité d'eau pour retrouver ses propriétés ; or, quand il est détérioré, il se remet très difficilement en équilibre avec l'humidité relative environnante. Une réhydratation progressive facilite la reprise d'eau et diminue considérablement la rétraction de ce matériau quand il est dégradé ; cependant, pour l'éviter complètement, il est nécessaire d'utiliser des cryoprotecteurs qui favorisent une rétention d'humidité lors de la dessication et qui, en outre, pourront régulariser le contenu en eau pendant la conservation ultérieure. La stabilité chimique et fongique de ces substances sera étudiée ainsi que leur effet sur les propriétés mécaniques du cuir.

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A PRELIMINARY STUDY OF THE USE OF INFRARED REFLECTOGRAPHY IN THE EXAMINATION OF WORKS OF ART ON PAPER

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SUMMARY

This paper focuses on the use of the Hamamatsu vidicon system at the National Gallery of Art for the examination of works of art on paper. Comparisons of results using various filters are described, as well as the possibility of identifying inks by their response to infrared (IR) with the different filters.

Introduction

The infrared vidicon system of reflectography as an examination method for works of art was devised by the Dutch physicist Van Asperen de Boer. It was developed specifically for the study of paintings and as an improvement over infrared photography. Van Asperen first described the method in 1966, using the Barnes Infrared Camera (designed to record emmitted heat) to record reflected infrared radiation.[1] Further research produced infrared reflectography as it is known today: a television tube or infrared vidicon, that translates the infrared into a visible image. The vidicon is housed in a high resolution television camera that is equipped with a macro lens and an infrared filter that blocks out visible light. The vidicon thus detects radiation between the lower limit of the filter and the vidicon's upper limit of around 1900 nm.

Most if not all of the material published on infrared reflectography thus far has focused on the examination of paintings. With the availability of infrared reflectography equipment at an increasing number of museums in the United States, its applicability to the examination of works of art on paper is becoming apparent.

In comparison with paintings, drawings seem simpler, more spontaneous in conception and execution. Because of this spontaneity, whether actual or perceived, drawings can be deceptive, tempting even the careful observer into a reverie of mistaken expertise. The casual observer rarely considers that a drawing might be carefully composed and constructed of several layers. It is my intention to describe some of the work that has been done using the IR vidicon system as a means of examining and interpreting drawings and related materials.

Examination of a Raphael Drawing

Our first experience that emphasized the practical usefulness of infrared reflectography for studying drawings was the examination of a work newly acquired by the National Gallery of Art, which has been intermittently attributed to Raphael. The drawing (B-33,667), depicting the legend of St. George and the Dragon, is executed in brown wash with white highlights and black chalk underdrawing. The sheet had suffered substantial image loss due to overall water damage and surface abrasion, making it exceedingly difficult to discern details of the image even though the basic composition was known through related drawings and prints.

Using the various examination techniques available to us, little by little we learned more about the drawing: raking light revealed the deliberation with which the transfer process was executed; ultraviolet light revealed a hitherto unperceived design element - a faintly sketched woman with outstretched arms in the upper left. The identification of this figure as the princess in the St. George legend further enhanced the attribution to Raphael by relating the drawing to other works by him[2] (including our own panel painting) on the same theme. The infrared vidicon system was used in an attempt to see the underdrawing more clearly. In scanning the drawing with the camera, the black chalk drawing revealed refinements and alterations in the artist's preliminary rendering. Detail shots were taken of areas of interest by photographing the reflectogram on the TV monitor. A 4 x 5 format camera with a polaroid attachment was first used to determine the correct exposure using a polaroid film (Type 52), final shots were then taken with Kodak plus X film, and 8 x 10 black & white prints were then produced for our object file. Regular infrared photography using Kodak High speed infrared film and a Kodak #70 filter produced very similar results to the reflectogram.

The reflectograms showed the brown wash to be almost transparent to infrared and the black chalk to be a strong absorber of it. X-ray fluorescence analysis determined that these brown areas contained relatively high quantities of iron and manganese, the latter indicating that the brown is an earth pigment. The uncolored portions of the paper contain minor but significant quantities of calcium, adding to the reflecting power of the paper. This drawing, then, fits precisely Van Asperen de Boer's specifications when he says:

> In summary, an underdrawing when present may be revealed if in the spectral region concerned:
>
> a) the drawn lines differ sufficiently in reflectance from their background to provide a detectable contrast.
>
> b) the overlying paint layers do not hide the drawing.[3]

In this regard it might be mentioned that while the lead white highlights seem to disappear in infrared because of their reflectiveness in the white state, they appear dark when converted to lead sulfide which absorbs infrared.

Specifications of the National Gallery of Art System

The infrared vidicon system at the National Gallery of Art was acquired in 1981 and consists of a Hamamatsu series 1000-03 television camera inside of which is housed a Hamamatsu high resolution N214 infrared vidicon tube. The spectral response range of this combination is between 400 nm and approximately 1900 nm and has a horizontal resolution of 600 TV lines. A Nikon Micro Nikkor 55 mm f/2.8 lens is attached to the camera, and a rotatable filter wheel that can accommodate four filters simultaneously is located in front of the lens. The only filter used initially was the Kodak 87A. The camera control unit, in a separate console, has beam and target controls which respectively adjust current to the tube and tube sensitivity. This Hamamatsu system, however, possesses several additional features: a gain/offset expansion control (M1438) that changes video gain by a factor of 1 - 16 by altering the voltage supplied to the tube. Use of the gain/offset controls allows adjustment and expansion of a selected intensity range in areas where contrast is minimal. Another option with this equipment is the M1003 Intensity Display which displays the intensity waveform of an image area along a selected and moveable vertical line. While this has not been used to any extent thus far, it could have some interesting applications in gauging the relative amounts of transmission/absorption in specific areas of an art work. This option will be most useful when

our equipment is fully computer interfaced so that
quantitative data can be collected, stored, re-run and
analyzed. The image is viewed on a CONRAC 12 inch TV
monitor with its own focusing (for TV lines resolu-
tion), brightness and contrast controls. We use a 500
watt quartz-iodide lamp regulated at approximately 400
lux or less for works of art on paper.

Pigment Test Chart and Filter Testing

Having become familiar with the working capabilities
of the equipment at the National Gallery of Art, an
opportunity to use another vidicon system presented
itself. The equipment at the Art Institute of Chicago
bears little resemblance to that at NGA, but the
images produced, if not better, seemed clearer.* The
question arose as to whether our system's capabilities
had been optimized. Molly Fairies, an art historian
from Indiana University, Bloomington, and a collabor-
ator of Van Asperen de Boer's, came to the Gallery in
1981 to carry out a survey of 15th & 16th century
Northern European panel paintings using IR reflecto-
graphy. She brought with her her own equipment which
is "the same type as van Asperen's, and adapted and
tested in the same way... [to] match the present
published standard".[4]** When our equipment arrived,
M. Fairies adjusted it to compare results with her
own, but reviewing the material 2 years later there
seemed to be some doubt about the clarity of our
images as compared to hers. While still in Washington
Fairies, using her equipment, had produced four 3" x
4" photographs of the reflectograms of a pigment chart
prepared by members of the Freer Gallery of Art
Conservation Technical staff. The Freer group had
wanted to know whether reflectography would be more
helpful than regular IR photography in examining some
of their Oriental screens, so a chart containing some
pigments typical of Oriental paintings was made up.
The pigments were applied in a water soluble medium in
2 to 3 layers, in most cases concealing the black
cross underneath the painted square. Although compar-
ing photographs of reflectograms to actual images on
the screen is not scientifically accurate, it did give
us some idea of how our system was functioning. The
first test of our system with the chart also made use
of 5 filters to see if there was any perceptible
difference in penetration. Kodak gelatin filters 87A,
87B, 87C, and 87 were attached to our filter wheel.
We also tried out a glass filter that screwed onto the
lens front - a Hoya RM90. (See chart #1)

Initial testing was performed in a room where there
was little control of situational lighting and the
results showed some unexpected variations in pigment
penetration with different filters. In our second
test with the pigment chart the vidicon system was
moved to an area where the quartz-iodide lamp was the
only light source and where the equipment could be
set-up and not moved by other Gallery staff. The
results with the different filters evened out consider-
ably and indicated to us that our system could be made
to function on a par with other standardized systems -
if proper conditions were established. In this second
test we also included reflectograms using no filter
and viewed with the naked eye (some of the crosses
were not completely concealed). As our results using
the 87A filter were comparable to M. Fairies, they are
recorded as one on the chart. Exceptions are de-
scribed as follows. Our observations seem to indicate

*The Art Institute of Chicago system consists of a
Dage, MTI Model 800 TV camera and a Canon 25-100 mm
manual zoom lens, f/1.8. This system uses the
Hamamatsu N156 IR vidicon and a Kodak 87C filter
screwed into the lens front.

**Molly Fairies' equipment consists of a Grundig TV
camera with controls set at 737 linear central
resolution, a 36 mm Zoomar macro lens, f/2.8. This
system uses a Hamamatsu N214 IR vidicon tube and a
Kodak 87A filter located between the macro lens and
the TV camera.
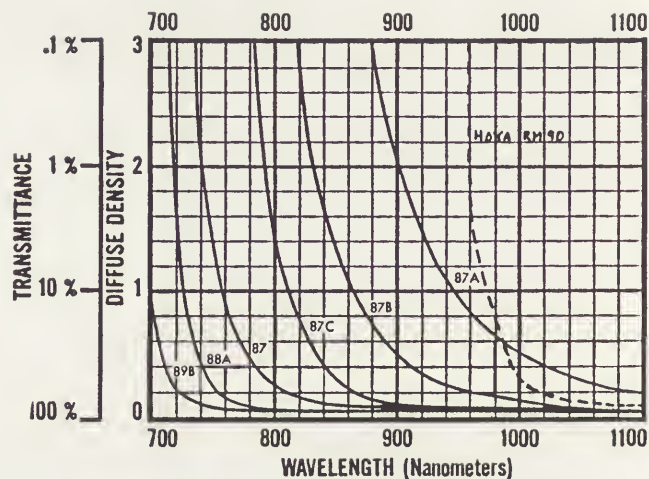
1. Transmission curves for Kodak filters taken from
Kodak Filters for Scientific and Technical Uses, 1976.
The Hoya curve is superimposed from manufacturer's
specifications.

that under optimal conditions, the filters tested did
not significantly alter the infrared penetration ofthe
pigments on the chart. There are some perceptible
differences however. Fairies 87A seemed to test
slightly better in iron oxide and litharge. Interest-
ingly, during the period between her test and ours,
the litharge seems to have significantly darkened
(PbO) and therefore is probably absorbing more of the
infrared than it did earlier. Smalt seems to be
penetrated less well with 87A than the other filters.
The penetration of finely ground azurite was question-
able and so was rated at 0; ultramarine was not
penetrated. Even though the system theoretically can
penetrate these blue pigments, the variables of
pigment thickness and particle size still present
barriers to penetration.

The result of using "no filter" was surprising in that
it shows that within a certain range of colors,
infrared penetration with no filter is as good or
better than with any of the filters used, except in
the case of iron oxide red. (See chart #2)

Examinations Using 3 Filters

The results of the pigment test chart didn't explain
the increase in "clarity" perceived in some vidicon
systems. However, when we began examining drawings
using the different filters (by simply rotating them
in the filter wheel), two things became apparent: 1)
The visual image on the monitor was higher in contrast
using filters 87 and 87C than 87A. (This makes sense
when you look at the filter chart since they are
admitting more light closer to the visible spectrum.)
While we could perceive no vast difference in the
amount of information gained, it was a matter of
seeing what was there. The image was easier to "read"
on our system with the 87C or 87 filters.   2) With
the ability to quickly and easily change filters it
became apparent that some inks were made visible (or
invisible) depending on the filter used.

We were interested in identifying the brown ink
applied with pen and the brown wash used in a drawing
by George Romney, Lady with a Lyre (NGA Held
Collection 70/12). The drawing was examined with
three filters. With the 87A filter the dark washes
became virtually invisible, showing only the fine line
pen, leading us to believe there were two inks
present. The other two filters, 87C and 87, however,
showed progressively more of the background and

PENETRATION OF PIGMENTS USING INFRARED VIDICON SYSTEM
AT NATIONAL GALLERY OF ART

	Hoya RM90	Kodak 87A	Kodak 87B	Kodak 87C	Kodak 87	No Filter	Naked Eye
Iron Oxide Red	+	+	+	+	0	0	0
Vermilion	0	0	0	0	0	+	0
Red Lead	+	+	+	+	+	++	+
Iron Oxide Yellow	+++	+++	+++	+++	++	+++	+
Orpiment	++	++	++	++	++	++	++
Litharge	0	+	+	+	+	+	0
Azurite (coarse)	++	+++	+++	+++	++	0	0
Azurite (fine)	0	0	0	0	0	0	0
Prussian Blue	0	0	0	0	0	0	0
Indigo	++++	++++	++++	++++	++++	0	0
Ultramarine	0	0	0	0	0	0	0
Smalt	+++	+++	++++	++++	++++	0	0
Shell White	+	+	+	+	+	0	0
Lead White	0	0	0	0	0	0	+
Clay White	++	++	++	++	++	0	+
Malachite (coarse)	0	0	0	0	0	0	0
Malachite (fine)	0	0	0	0	0	0	0

KEY: ++++ = strong   +++ = moderate   ++ = weak   + = trace   0 = opaque

2. The pigment chart used to obtain these results was provided by the Conservation Technical staff of the Freer Gallery of Art, Washington, D.C.

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contour washes. X-ray fluorescence analysis revealed that wash areas as well as fine line areas contain significant amounts of iron. Slight amounts of manganese were noted in some of the wash areas tested. The analysis was inconclusive but indicated that there wasn't a significant difference between the pen lines and the washes done with a brush. Looking more closely at the reflectogram, it was noted that some of the pen lines did exhibit the same characteristics as the wash. Further examination with a stereo binocular microscope revealed something interesting about this very spontaneous-looking drawing by Romney: most of the pen lines visible in the reflectogram were quite carefully or deliberately covering over lines of graphite pencil! Other fainter graphite lines that had not been re-traced with pen also were found on the reflectogram. We concluded that this ink was probably iron gall, perhaps with some admixture of small amounts of another pigment in the wash. Had we based our assessment of the results on the filter above, we would have reached the wrong conclusion that two different inks were present. (See photo)

Some 18th C. writing samples and several other drawings known through analysis to be iron gall ink were examined with 3 filters and were found to exhibit the same characteristics as the Romney ink – that is, faint to invisible with the 87A filter and progressively more visible with 87C and 87. We concluded that this phenomenon is typical of old brown iron gall ink, as opposed to fresh iron gall ink in its black state. Known samples of filtered bistre and sepia were also examined with the three filters – the bistre remains transparent to infrared with all three filters and sepia remains opaque with all three (as would a carbon ink). By using only the 87A filter we would not be able to differentiate iron gall from bistre. Though this examination procedure may be a good means of differentiating between these three often confused inks, it is a good policy to have standard samples of these inks as well as a brown earth to use for comparison. (The brown earth pigments, in varying degrees appear more transparent but still visible with all three filters.) It should also be stressed that good analytical support data on these standard inks and pigments is necessary in order to get a better idea of the elemental differences among these inks and when possible to sample unknowns from actual drawings and documents for comparison. Initial x-ray fluorescence analytical work done at the National Gallery of Art

by Barbara A. Miller indicates that all three inks may contain iron but in vastly differing amounts, i.e. iron gall inks usually contains 100% to 350% more iron than the surrounding bare paper, while sepia and bistre samples may contain from 0% to 20% more iron than the paper. Some preliminary tests done at the Fogg Art Museum in Cambridge, Massachusetts, show a clear preponderance of iron and free sulphur in iron gall ink. Although bistre and sepia are more difficult to characterize, magnesium and nitrogen are consistently recorded in sepia, while neither element is seen in bistre. (The Fogg studies used the scanning electron microscope with energy dispersive x-ray analyses, x-ray photoelectron spectrography and auger electron spectroscopy.) Another important observation made in the Fogg study is that it is dangerous to judge or label an ink as one or the other of these three simply on appearance. Almost consistently, using 5 Tiepolo drawings as examples, inks which were thought to be bistre or sepia were found to have the constituents of iron gall ink.[5]

In collaboration with the conservation and curatorial staff of the Art Institute of Chicago, the author examined 12 pastels by Edgar Degas using their reflectography equipment. The pastels, most of which had not been unframed since their acquisition by the Institute, revealed many changes. Regardless of whether these pastels were worked over monotypes as was customary for Degas, or were done in pastel alone, many of them showed compositional changes and pose alterations from one stage of pastel drawing to another. The ability of infrared reflectography to penetrate (at least to some degree) a medium that the author had feared would be too opaque and dense was encouraging. Success with these pastels indicates the usefulness of this examination technique for a wide variety of works of art on paper.

Conclusion

In our work, then, infrared reflectography as a tool for the examination of works of art on paper has proved to be of major significance in three areas:

1. more clearly revealing underdrawings – usually done in a carbon or graphite material preliminary to final applications of washes, etc.

The three reflectograms above show the effects (from left to right) of Kodak filter 87A, 87C and no filter on a detail of a drawing by George Romney, Lady with a Lyre.

2. revealing changes or alterations in the artist's original conception.

3. revealing differences in infrared reflection of materials such as inks so that identification of these materials may be possible.

It has been noted that there is a variety of combinations of vidicon systems in use. From our experience it would seem necessary to "optimize" the equipment by: 1) getting in a knowledgeable technical representative to make sure that optical resolution is attained, and to acquaint the user with all of the options and nuances of the equipment. 2) Testing the system with standards of known pigments, inks, etc., and if possible comparing it with the results of another vidicon system. Our system is capable of easily using a series of filters and we have found this useful for our purposes. Whether others will find this an accomplishable or desireable feature with the equipment remains to be seen. However, it is absolutely necessary when reporting results that the type of equipment including the filter type used be reported.

With respect to infrared reflectography as a tool, one of its major assets in addition to being superior to infrared photography as far as pigment penetration is concerned, is simply its ease of access and use. This is an important feature whether it is a painting or a drawing that is being examined, for it means that more objects will be given the kind of in-depth scrutiny

they deserve. In the long run this means a tremendous increase in the understanding of the materials and techniques of drawings and other works of art on paper.

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ANALYSE "IN SITU" PAR MICROSONDE RAMAN LASER D'UNE COUCHE PICTURALE A TRAVERS UN SUPPORT TRANSPARENT

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RESUME

En permettant d'identifier "in situ" par leur spectre
caractéristique de très petites inclusions étrangères,
transparentes ou opaques, au sein d'un milieu transpa-
rent, la microsonde Raman laser s'est révélée être une
technique de microanalyse véritablement non destruc-
tive.
Cette technique nous a paru particulièrement bien
adaptée à l'étude des oeuvres d'art, en particulier
pour l'analyse de certaines couches picturales inclu-
ses dans une matrice transparente telle que glaçure,
vernis, liant ou adhésif de protection.
De telles couches picturales sont en effet difficile-
ment accessibles par d'autres techniques d'analyse qui
risquent de détruire partiellement l'oeuvre conservée.
La possibilité offerte d'identifier la composition de
ces couches picturales directement à partir de la sur-
face, dont nous montrerons quelques exemples, apporte
une solution nouvelle aux difficultés rencontrées
jusqu'à présent dans ce domaine.

I - INTRODUCTION

Rappelons brièvement le principe de la méthode d'ana-
lyse par microsonde Raman laser, la description de
cette technique ayant déjà fait l'objet de nombreuses
publications antérieures (1 à 3).

La méthode consiste à illuminer ponctuellement, à tra-
vers l'optique d'un microscope classique de fort gros-
sissement, un fragment de matière à l'aide d'une radia-
tion monochromatique ν_0 fournie par un laser. Une par-
tie de la lumière excitatrice est diffusée par l'échan-
tillon.

L'examen de cette lumière diffusée par des moyens
spectrométriques, montre de part et d'autre de la fré-
quence ν_0 de la radiation principale (ou raie Rayleigh)
la présence de radiations de très faible intensité et
de fréquences $\nu_0 \pm \nu_n$ (effet Raman).

Les écarts en fréquences observés ν_n sont égaux aux
fréquences des vibrations des atomes des édifices molé-
culaires constitutifs de l'échantillon.
La mesure de ces écarts exprimée en cm^{-1} par la posi-
tion des raies sur les spectres par rapport à la raie
principale prise pour origine, permet d'identifier la
structure du ou des composés en présence et par suite
de déterminer ponctuellement la composition du frag-
ment de matière à analyser.

Une focalisation précise du faisceau du laser peut être
obtenue et permet de circonscrire la zone de l'analyse
à une surface inférieure à un micron carré.
Contrairement à d'autres techniques de microanalyse, la
mesure s'effectue à l'air libre, sans modification ni
préparation particulière de l'échantillon.
La puissance du faisceau Laser étant très faible, on
peut effectuer ces mesures dans des conditions où
l'échantillon ne subit pas de dégradation (thermique
ou photochimique) ce qui rend cette méthode non des-
tructive.
En utilisant des microprélèvements de la taille de quel-
ques microns, cette technique nous a permis d'identi-
fier divers composés organiques ou minéraux rencontrés
dans les couches picturales de nombreuses oeuvres
conservées (4 et 5).

La microsonde Raman laser permet aussi d'identifier
"in situ" ces couches picturales, sans qu'aucun prélè-
vement ne soit alors nécessaire. Cette possibilité
nous a paru particulièrement précieuse, notamment,
lorsque ces couches ne sont pas directement accessibles
à partir de la surface et se trouvent "incluses" dans
une matrice relativement transparente, résultant de
l'adjonction aux pigments eux-mêmes de liants, de di-
verses émulsions ou de différents vernis et glaçures.

Classiquement, l'étude complète de ces couches pictu-
rales se fait par le prélèvement d'une très petite
"écaille de peinture", échantillon que l'on étudie gé-
néralement en coupe au moyen de différentes techniques
microchimiques ou spectrométriques. Les résultats de
ces examens permettent l'identification précise de la
plupart des composés organiques ou minéraux rencontrés
(5). Ces examens présentent, cependant, l'inconvénient
majeur de ne pouvoir être répétés aussi souvent qu'on
le souhaiterait, le risque étant grand, en multipliant
les prélèvements, d'endommager irrémédiablement l'oeu-
vre d'art étudiée.

Il arrive aussi que certaines peintures soient simple-
ment recouvertes d'un matériau de protection transpa-
rent posé en surface, matériau qu'il n'est pas possible
ou simplement pas souhaitable d'enlever pour une bonne
conservation de l'oeuvre.

Tel est le cas de certains fixatifs naturels ou de
synthèse (employés, par exemple, pour la protection
de peintures murales), ou de revêtements adhésifs de
protection (comme ceux employés dans la conservation
de papiers anciens) ou plus simplement encore de verres
d'encadrement servant à la protection de tracés fragi-
les tels que des dessins au pastel.

Pour chacun des cas qui viennent d'être évoqués, la
possibilité offerte par la microsonde Raman Laser
d'effectuer des analyses "in situ" (analyses dont les
résultats s'expriment en terme de composés) semblait à
juste titre, particulièrement prometteuse. Nous l'avons
expérimentée avec succès sur quelques cas précis dont
nous donnons ici les résultats en les accompagnant des
observations que nous avons pu faire au cours de l'ex-
périmentation.

Malgré certaines limitations actuelles de l'instrumen-
tation, limitations qui seront précisées, l'ensemble
tend à montrer les très grandes possibilités d'inves-
tigation offertes par cette méthode et laisse entrevoir
un vaste champ d'applications. Dans le domaine particu-
lier de l'étude et de la conservation des oeuvres d'art,
une grande partie de ce champ reste encore à explorer.

II - MESURE "IN SITU" A TRAVERS UN ADHESIF TRANSPARENT DE PROTECTION ET DE RENFORCEMENT

On sait que certains papiers datant du 19ème siècle,
voire de l'époque contemporaine, fabriqués industriel-
lement à partir de pâtes chimiques blanchies de qualité
moyenne, résistent mal à l'action du temps. Des docu-
ments tels que des journaux ou périodiques, des affi-
ches, des correspondances publiques ou privées qui
constituent des sources historiques irremplaçables, ne
peuvent plus être consultés parce que trop fragiles. Le
papier qui leur sert de support est devenu dur, cassant,
prêt à se réduire en fragments dès la première manipu-
lation.

Afin de conserver ces documents et de permettre malgré
tout leur consultation, on a mis au point différents
procédés de consolidation dont le principe commun repose
sur l'adjonction d'un support de renforcement au docu-
ment fragilisé. Ce support souple et transparent peut
être fixé sur un seul côté du document. Parfois, il
renforce le papier sur ses deux faces. Le document est
alors, comme pris en sandwich entre deux feuilles adhé-
sives transparentes. On procède actuellement par lamina-
ge à chaud d'une résille faite d'un enchevêtrement de
fibres synthétiques (de type polyamide) fixée sur le
papier par l'intermédiaire d'un film adhésif double face
de faible épaisseur (également de type polyamide).

Le procédé est réversible et, si les circonstances
l'exigent, ce renforcement peut être retiré. Il s'agit

là cependant, d'une opération délicate qui ne peut être entreprise sans de sérieux motifs.

Il nous a donc paru intéressant d'étudier la possibilité d'effectuer à l'aide de la microsonde, une analyse "in situ" du document, c'est-à-dire à travers le support adhésif transparent lui servant de renforcement et de protection.

Pour un premier essai, nous nous sommes contentés d'effectuer quelques tests à l'aide de papiers que nous avons nous-mêmes colorés avec des crayons pastels du commerce de différentes couleurs. Nous avons ensuite analysé à la microsonde ces aplats de couleur, successivement, avant, puis, après renforcement du papier par l'adhésif.

Les spectres obtenus permettent d'identifier dans chacun des cas, le pigment utilisé sans ambiguïté possible Il s'agit d'un pigment outremer dans le premier cas (fig. 1, courbe d). On observe sur le spectre une raie caractéristique à 548 cm^{-1} due à l'ion S$_3^-$ et son premier harmonique à 1096 cm^{-1}. Dans le deuxième cas (fig. 2), on a pu identifier la couleur verte employée comme étant un mélange de bleu et de jaune. Le pigment jaune est un jaune de chrome dont le spectre présente une raie intense à 842 cm^{-1} correspondant à la vibration ν_1 de l'ion chromate CrO$_4^{3-}$.

Malgré un rapport signal sur bruit parfois moins favorable, le revêtement transparent posé en surface ne paraît donc pas devoir empêcher les mesures effectuées "in situ".

Notons que les spectres ont été obtenus en prenant soin d'illuminer sous le faisceau du laser, un endroit de la couche colorée libre de toute fibre polyamide, c'est-à-dire dans l'un des nombreux intervalles laissés libres par le réseau des fibres. Le réseau apparaît nettement visible à l'observation au microscope.

D'autres raies, qui ne sont pas présentées ici, ont pu être observées dans une partie éloignée du spectre. Ces raies qui sont situées vers 2880 cm^{-1} et 2920 cm^{-1} correspondent aux composés polyamides et, du fait de leur éloignement des autres raies, ne sauraient se superposer ni être confondues avec celles-ci sur les spectres.

III - MESURE "IN SITU" A TRAVERS UN VERRE DE PROTECTION

Nous avons effectué cette mesure de deux manières différentes. Dans un premier temps, nous avons étudié un dessin au pastel du début du XXème siècle, dont nous avons tenté de déterminer à travers sa vitre de protection, c'est-à-dire sans démontage de son encadrement, la composition de quelques-unes des couleurs employées.

Pour faire ces mesures, nous avons dû utiliser un objectif spécial de grossissement x 50 et de 6 mm de focale. Cet objectif "longue frontale" est nécessaire à la mise au point du faisceau du laser sur la couche picturale dont il n'est pas possible d'approcher l'objectif à cause de l'obstacle constitué par la vitre de protection.

L'ouverture numérique de 0,5 d'un tel objectif est inférieure presque de moitié à celle de l'objectif x 100, de distance frontale d'une centaine de microns, habituellement utilisé. Cette ouverture moindre entraîne une perte sensible du flux de la lumière diffusée collectée vers le spectromètre.

En dépit de ces conditions moins favorables, le spectre que nous avons pu relever pour la couleur bleue dominante du tableau fait apparaître des raies à 257 cm^{-1} et à 548 cm^{-1} qui caractérisent sans difficulté la présence d'un pigment à base d'outremer (fig. 1, courbe c).

D'autres mesures réalisées en plusieurs autres endroits du tableau ont permis d'identifier de la même façon plusieurs autres pigments. On observe, malgré tout, sur les spectres un rapport signal sur bruit nettement moins élevé que sur le spectre d'échantillons semblables relevés à l'air libre.

Le seul obstacle aux mesures que nous ayons réellement rencontré vient de la difficulté d'effectuer une analyse dans la partie centrale du tableau, ceci en raison des dimensions de la platine du microscope. Celle-ci ne permet pas en effet actuellement le débattement suffisant qui serait nécessaire pour positionner le faisceau au centre de tableaux de trop grandes dimensions.

Dans un deuxième temps, nous avons tenté d'effectuer une série de mesures systématiques à partir d'un échantillon de composition connue et en recouvrant cet échantillon d'une épaisseur de verre de plus en plus grande.

Nous avons choisi d'utiliser une petite quantité d'outremer composée de quelques grains d'une centaine de microns, amas que nous avons recouvert successivement d'une, puis de plusieurs lames de verre.

On observe sur les spectres une diminution progressive de l'intensité des raies. Cet affaiblissement semble être directement proportionnel à l'épaisseur du verre recouvrant l'échantillon.

Pour quatre épaisseurs de lames   correspondant à environ 3,6 mm d'épaisseur de verre, le spectre présente encore ses raies caractéristiques à 548 cm-1 et 1096 cm-1. Nous n'avons pu aller au-delà, ne disposant pas des objectifs nécessaires, c'est-à-dire ayant à la fois une plus longue distance frontale et une ouverture numérique suffisante.

IV - ANALYSE "IN SITU" D'UN MICROPRELEVEMENT CONSERVE DANS UN LIQUIDE TRANSPARENT DE MONTAGE

La microsonde Raman laser permet des analyses très ponctuelles grâce à la focalisation possible du faisceau du laser sur des surfaces aussi petites que quelques microns, voire quelques dixièmes de micron. Elle donne donc la possibilité d'analyser des microprélèvements de tailles très réduites. De tels prélèvements, quand ils sont possibles, peuvent être considérés comme non destructifs, car les traces laissées sur l'oeuvre conservée restent totalement invisibles à l'oeil nu.

La difficulté réside dans le stockage et le transport d'aussi petits échantillons depuis le lieu du prélèvement jusqu'au laboratoire où s'effectuent les mesures. Nous avons choisi d'utiliser un liquide de montage permettant d'inclure ce micro-échantillon dans un milieu transparent. Les caractéristiques spectrales de ce milieu de montage ne doivent évidemment pas modifier l'observation ou entraver les mesures.

Plusieurs liquides de montage ont été essayés. La plupart présentent l'inconvénient d'être très fluorescents, ce qui gêne considérablement les mesures. C'est le cas, en particulier, du baume du Canada et du collodion habituellement utilisés par les microscopistes.

Un autre essai réalisé à partir d'un liquide de montage synthétique (liquide Eukitt) nous a donné de meilleurs résultats. Ce liquide de montage au temps de durcissement très court (20 minutes environ) est employé pour la conservation des colorations fragiles. Son indice de réfraction voisin de 1,5 à 20°C est proche de celui du verre des lames et lamelles utilisées en microscopie optique. Aucun phénomène de fluorescence n'est observé dans le relevé des spectres.

Nous présentons (figure 1, courbe b) le spectre obtenu à partir d'un grain d'outremer aux dimensions de 40 microns environ, inclus sur une lame de verre dans ce liquide de montage. On identifie aisément sur la courbe les raies caractéristiques de l'outremer situées à 258 cm^{-1}, 548 cm^{-1} et 1097 cm^{-1}, en dépit d'un rapport signal sur bruit très légèrement inférieur à celui que l'on observe pour le même échantillon disposé à l'air libre sur une lame de verre.

Cette analyse réalisée "in situ" apporte donc une solution satisfaisante aux problèmes posés par le transport de micro-échantillons devant être conservés. C'est le cas des micro-prélèvements réalisés sur des oeuvres d'art fragiles telles que les manuscrits ornés du Moyen Age, documents précieux pour lesquels les prélèvements

ne peuvent être effectués qu'en nombre très limités et
doivent être autant que possible conservés.

V - IDENTIFICATION "IN SITU" D'UN JAUNE D'ANTIMOINE

Certains pigments dits "d'émail" dus aux fabrications
des verriers et notamment des verriers vénitiens ont
été utilisés dès la fin du XVe siècle par les peintres
et certains enlumineurs de manuscrits.

Ces pigments résultent du chauffage lent jusqu'à la
fusion et, après refroidissement, du broyage d'un mé-
lange composé d'un oxyde métallique, de silice ou
d'alumine et d'un fondant (généralement à base de
potasse).

Le bleu de smalt ou zaffre, appelé parfois "bleu d'é-
mail" est l'un de ces pigments. Il est à base d'oxyde
de cobalt.

Le jaune de Naples, dont la fabrication en Italie fut
longtemps tenue secrète,est à base d'oxydes d'antimoine
et de plomb. La composition de ce dernier pigment ne
fut connue qu'à la suite des travaux de FOUGEROUX de
BONDAROY, lequel devait proposer plusieurs recettes
pour sa fabrication. Ces recettes se multiplièrent
encore par la suite, tant et si bien qu'on a pu dire
que le jaune de Naples correspondait plus à une teinte
de jaune qu'à une composition bien définie.

Cette teinte réputée être plutôt jaune clair et légère-
ment verdâtre s'observe cependant avec de larges varia-
tions dans une gamme pouvant s'étendre du jaune orangé
au jaune le plus vif. Selon certains auteurs, de telles
variations résultent d'un excès plus ou moins important
d'oxyde de plomb. Elles peuvent aussi provenir de dif-
férences dans les températures de cuisson ou encore de
l'addition au mélange de faibles quantités de fer ou
d'étain.

Faisant suite précisément à une étude sur le jaune
d'étain que nous avions entreprise, nous avons cherché
à analyser différents jaunes d'antimoine d'abord à
partir d'échantillons de référence, puis dans un deuxiè-
me temps, là où ces jaunes sont le plus souvent rencon-
trés, c'est-à-dire dans le décor des faïences stanni-
fères.
Nous présentons ici les premiers résultats obtenus à
l'aide de la microsonde Raman Laser, espérant ainsi
contribuer à une meilleure connaissance de cette fa-
mille de pigments dont l'emploi s'est étendu à la
peinture et à la décoration, notamment de certains
documents graphiques.

La figure 3 (courbe b) montre le spectre obtenu "in
situ" sur le jaune clair d'une faïence stannifère de
Nevers à travers la couche d'émail (coloration jaune
dite "jaune citrin" par les historiens de la faïence
de Nevers). Ce spectre révèle la présence d'un anti-
moniate de plomb. Il peut être comparé à celui d'un
échantillon de référence de jaune d'antimoine (courbe
a), échantillon que nous avons identifié auparavant
par diffraction de rayons X comme étant un mélange
d'antimoniate de plomb de formule $Pb_{2,5}.Sb_{1,5}.O_7$ et
et d'oxyde d'étain SnO_2.
Les raies observées à 332 cm^{-1}, 455 cm^{-1} et 513 cm^{-1}
correspondent aux fréquences de vibrations de l'ion
SbO_4, celles observées à 141 cm^{-1} à PbO et celles
à 637 cm^{-1} et 780 cm^{-1} à SnO_2.

D'autres mesures ont été effectuées sur ce même décor,
notamment sur une couleur plus orangée (dite "jaune
profond"). Les spectres révèlent aussi la présence
d'antimoniate de plomb. On observe cependant quelques
différences notamment dans l'intensité des raies.
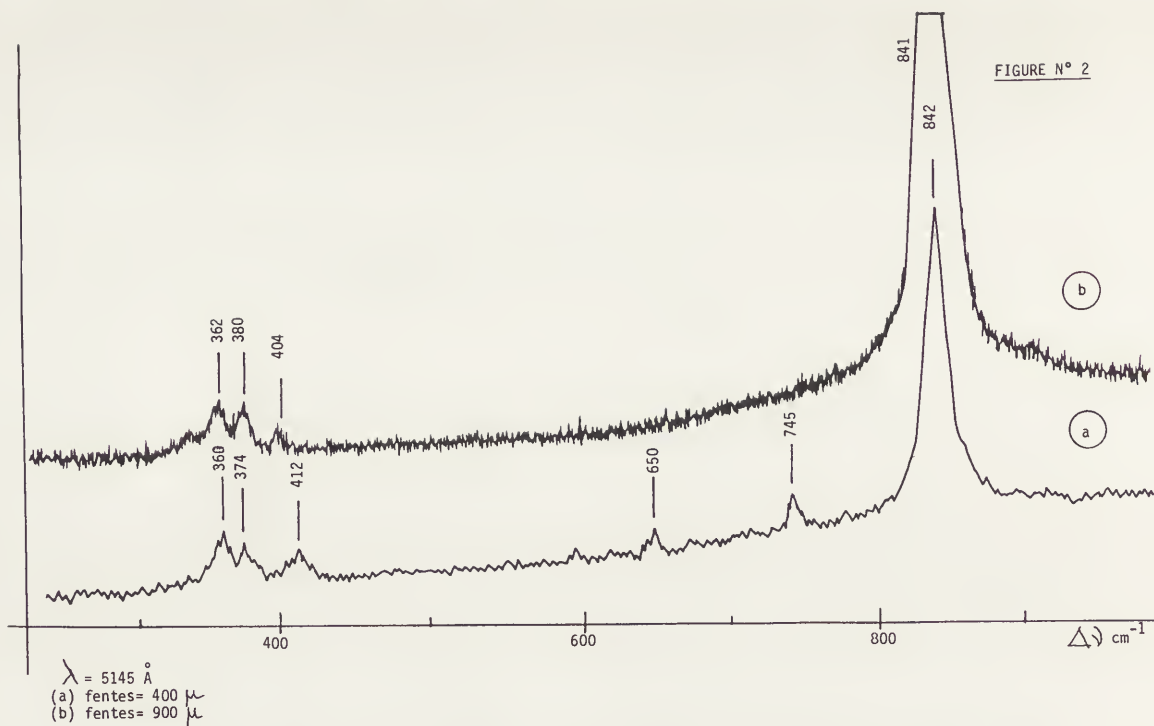L'interprétation de ces spectres est en cours.

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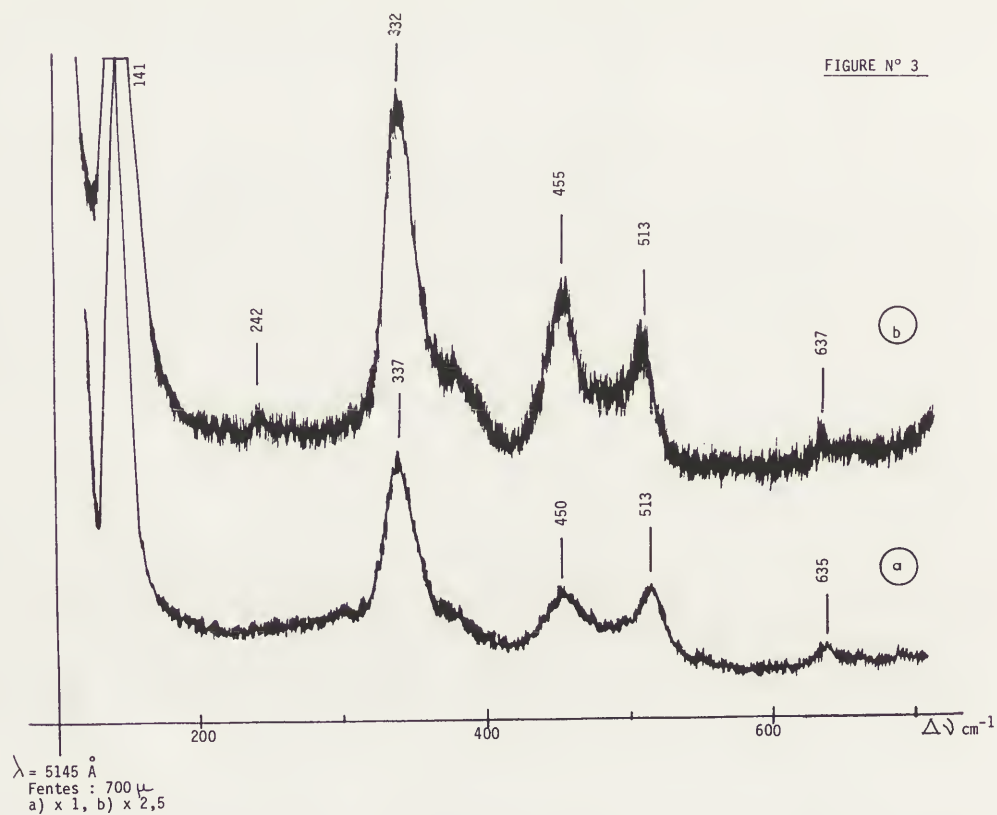29 (1984).
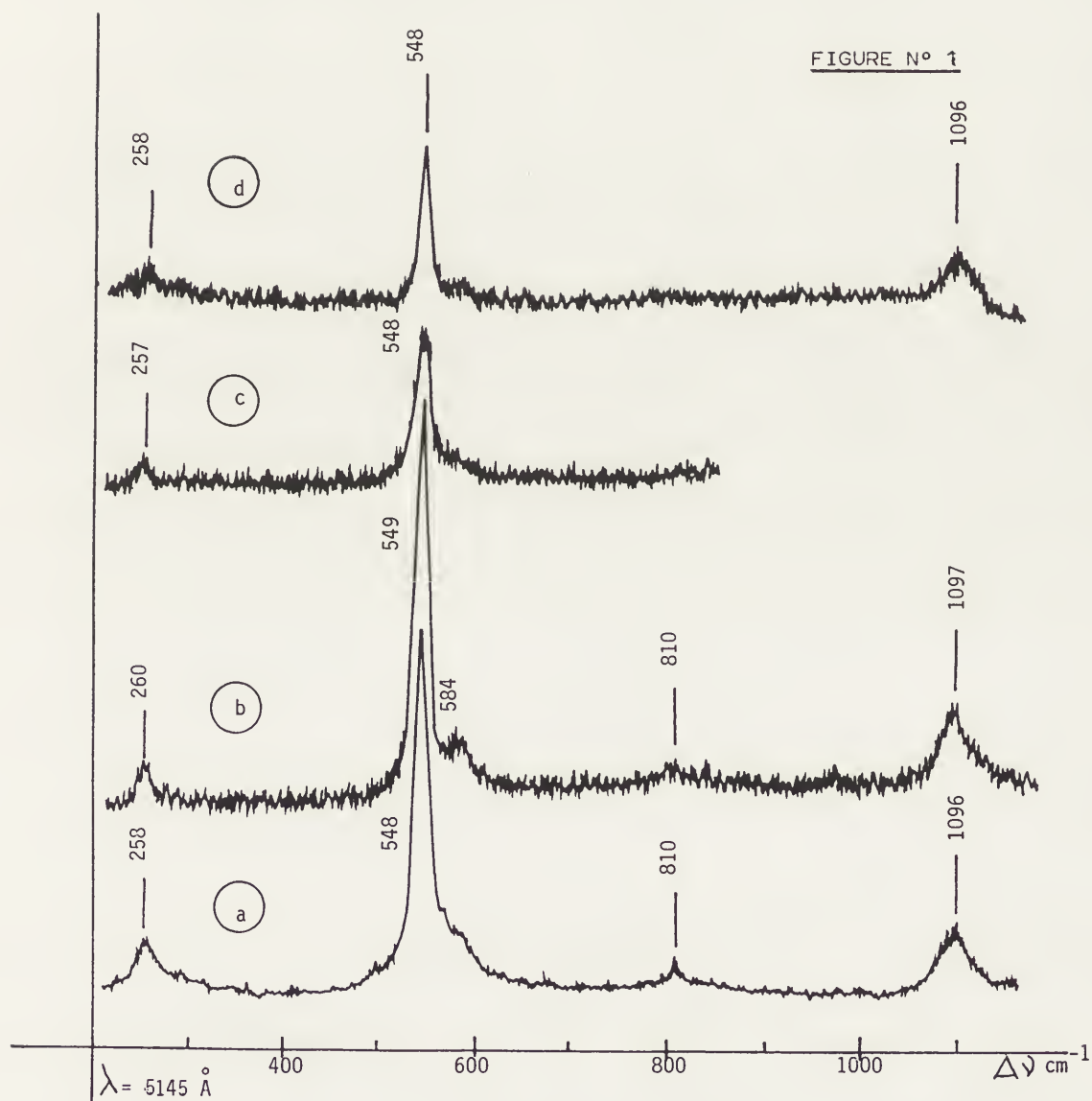
SPECTRE RAMAN DU BLEU OUTREMER

a) Echantillon de référence , b) Micro-échantillon de référence (40 μ),
conservé sur lame de verre et fixé à l'aide d'un liquide de montage transparent,
c) couleur bleue d'un dessin au pastel (début XXe s.) identifiée à travers la vitre
de protection de l'encadrement, d) Tracé bleu sur papier (tracé au pastel) identifié
à travers l'adhésif transparent de protection et de renforcement (Cerex et Bifix)

841
842
b
362
380
404
a
360
374
412
650
745

400   600   800 $\Delta\vartheta$ cm^{-1}

λ = 5145 Å
(a) fentes= 400 μ
(b) fentes= 900 μ

SPECTRE RAMAN DU JAUNE DE CHROME (Pb CrO$_4$)

a) Echantillon de référence , b) Tracé vert sur papier (tracé au pastel) et recouvert d'un adhésif transparent de protection et de renforcement (Cerex et Bifix).

332
141
455
513
242
b
337
450
513
637
635
a

200   400   600 $\Delta\vartheta$ cm^{-1}

λ = 5145 Å
Fentes : 700 μ
a) x 1, b) x 2,5

SPECTRE RAMAN DU JAUNE DE NAPLES (Pb$_{2,5}$. Sb$_{1,5}$. O$_7$)

a) Echantillon de référence, b) Décor de faïence stannifère (Nevers, début XIXe s.)

EXPERIMENTS ON THE RESTORATION OF DISCOLOURED BLACK-AND-WHITE PHOTOGRAPHS IN CHEMICAL SOLUTIONS

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SUMMARY

The conservation of photographic materials is emerging as a field of specialization. While addressing areas of concern common to the preservation of most types of cultural property—such as environmental criteria for storage and display, examination and identification, emergency procedures, fumigation, and the development of apprenticeship programs—the conservation of processed photographic materials also requires separate methods and specialized care. This paper reviews restoration treatments applicable to photographs and describes experiments on the restoration of discoloured black-and-white photographs in chemical solutions. Test procedures are outlined that allow a fair assessment whether a given photograph will survive such treatments.

The field of inquiry concerned with the conservation of photographs is conveniently divided into three groups of activities, each of which requires a different expertise:

1. The application of conventional and established prints and drawings conservation techniques to photographs.

2. The duplication of negatives and transparencies, and the copying of positive reflection prints.

3. The chemical restoration in aqueous solutions of faded or discoloured black-and-white negatives or prints.

While certain conventional conservation treatments are performed regularly in practice, they are almost exclusively adopted from skills developed elsewhere. Examples are the cleaning of photographs in the dry or wet state; removal of a picture from the support onto which it is mounted; the flattening of curled-up films or prints; the laying down of photographs onto a new, stable support; and sometimes retouching. Knowledge and skills in these areas have flowed generally in one direction: from prints and drawings conservation towards photograph conservation. However, the equation of photographic prints with graphic works of art on paper proves to be an inadequate premise when considering more complex treatments. The fundamental distinction here is one of structure: most photographic materials consist of two separate layers which react differently to changing environmental conditions, especially to changes in relative humidity. Consequently, certain restoration techniques are typical to photographic materials. There is, for example, the transfer of the image layer from a deteriorating support onto a new and stable base. Requiring considerable manual skill, it is usually done with transparent materials, i.e. negatives on glass or plastic film (1), and also with colour transparencies (2, 3).

A characteristic property of a processed photographic negative or transparency is its capability of being duplicated onto an identical material with faithful retention of tonal range and detail. Likewise, the copying of a black-and-white print, using a suitable film in a camera, can produce a negative from which an exact copy print can be obtained. The successful execution of such activities requires special skills and understanding of sensitometry as it applies to the theory and practice of what is technically known as tone reproduction. They do not constitute a restoration procedure, as the term restoration should be used only for work on an original image. However, the ability to faithfully duplicate an original presents a singular opportunity to preserve that original.

The chemical treatment of discoloured, or faded, black-and-white negatives and prints is a type of restoration procedure uniquely applicable to photographic silver images. While the fading of organic dyes in processed colour photographic materials, caused by hydrolysis or oxidation of dyes, appears to be irreversible, discolouration in processed black-and-white materials is initiated by an oxidation of elemental silver, which is generally followed by one of three subsequent reactions:

(i) silver ions can migrate through the binding medium, which has, for example, been observed in albumen prints and silver gelatin materials;

(ii) silver ions can react with available anions to form stable silver salts; or

(iii) silver ions can be reduced to a modification of elemental silver which appears orange-red in colour.

While a lateral migration of silver ions inside a gelatin layer cannot be demonstrated easily, the upward migration is shown by the appearance of a blue metallic sheen in the high density, or shadow, areas of a print or negative. It is easily noticed when letting the incident light reflect from an affected area. The formation of a silver sulfide transfer image in the baryta layer of a print, i.e. below the image bearing gelatin layer, which was first observed by Weyde (4), can be interpreted as proof of a downward silver ion migration away from the surface through the emulsion layer.
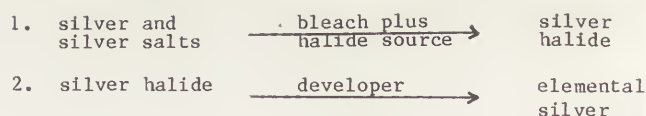
The blue metallic sheen likely consists of a thin layer of elemental silver formed around silver sulfide nuclei. Procedures to remove it chemically have been published by Henn, Crabtree and Russell (5) and by Weyde (6). Strictly speaking, such treatments are chemical restoration procedures, as would be the cleaning of tarnished daguerreotypes using acidic thiourea solutions or potassium cyanide. It is also possible to selectively remove the orange-coloured modification of elemental silver in chemical solutions. All these methods have in common that a certain amount of elemental silver, the image-forming substance, is irreversibly removed from the picture. Other methods attempt to increase, or to reduce, the silver density and to convert unwanted silver salts—products of deterioration reactions—back into black elemental silver. Such methods have been known in principle since the 19th century. They are referred to as intensification or reduction, when applied to negatives, and bleach and redevelopment with respect to paper prints. This presentation proposes to outline systematic attempts to develop safe and reproducible chemical restoration treatments of the latter kind. These treatments are directed only towards the image silver and must not affect the binding medium or the support.

Our interest in examining the possibility of restoring discoloured black-and-white photographic prints was kindled a few years ago when we investigated the reaction of such prints towards compounds that are commonly used in prints and drawings conservation for the bleaching of paper (7). Of four different bleaching agents—calcium hypochlorite, chlorine dioxide, hydrogen peroxide and Chloramine-T—only the latter had little appreciable effect on the silver density of contemporary developed-out prints (D.O.P.), but a

more drastic reduction in density was observed with printed-out paper (P.O.P.) images, such as salt prints, albumen prints and silver gelatin P.O.P. While calcium hypochlorite showed a devastating effect on all silver materials (P.O.P. and D.O.P.) as well as on the gelatin layer of carbon prints and Woodbury-types, the binding agent in albumen prints remained intact. Its silver density, however, was reduced considerably during four bleaching experiments of five, fifteen, thirty and sixty minutes duration. Chlorine dioxide, during reaction times of two, five, fifteen and thirty minutes, had a density-reducing effect which was about equally strong for printed-out and developed-out silver images. It seemed obvious to attempt conversion of the bleached silver images back into black silver using a photographic developer. While some test samples of contemporary developed-out papers responded well to such treatment, the printed-out papers, especially albumen prints, gave unsatisfactory results. Three observations with regard to printed-out papers are relevant: densities after development of a bleached image often exceeded the original values; image tones ranged from pink to brown to green; and there was a noticeable increase in graininess. Experiments performed in other projects confirmed to us that printed-out photographs, especially albumen prints, are not suitable for treatments which require bleaching and redevelopment of the image silver.

The results from these experiments led us to a more systematic investigation of the possibility of restoring discoloured black-and-white photographic images in chemical solutions. While there is no lack of formulae in the published literature, there appears to be little published experimental data about which formula is applicable for which type of discolouration on which type of image. Wall (8) published a critical résumé of all known methods of intensification and reduction of negatives in 1927, with a few hundred references. Another classical text, published in 1920 by Stenger (9), reviewed the restoration and copying of positive images. Here too, a large collection of formulae can be found, but no data are presented that would show their effectiveness. Methods for the intensification and reduction of negatives seem to have been studied more intensively than those for the restoration of discoloured prints by bleach and redevelopment. Correction of the negative, being a unique object and therefore more valuable than a print, has attracted more attention than the improvement of prints. Crabtree and Muehler reviewed intensifying and reducing solutions for motion picture film (10). Heymer discussed the reduction of contrast in small format negatives with simultaneous improvement of graininess (11). An intensifier for very weak negatives which gives exceptional density increase was proposed by Muehler and Crabtree (12). It was recently used to improve image characteristics in aerial photographic negatives of low density and contrast (13). The effect of several reducers and intensifiers on the resolving power of photographic emulsions was studied by Perrin and Altman (14). The chemical reactions that take place in various procedures are rather complex. Photographic reducers generally convert image silver partially into soluble salts, such as silver chloride (soluble in a thiosulfate solution), silver sulfate or silver ferrocyanide, which are subsequently removed from the image. During intensification reactions, elementary silver may be added to the original image silver; or dark-coloured silver complexes with other metals or with organic compounds may be formed; or the structure and size of the silver grains may be altered so as to produce an increase in density.

By contrast, the principle of a chemical restoration treatment for discoloured photographic prints is simple: all image silver in whichever modification, and all silver compounds in whatever form they may be present as products of deterioration, are uniformly converted into a silver halide which is then chemically reduced to black elemental silver. This is summarized in the following schema:

1. silver and   bleach plus   silver
    silver salts   —— halide source ——→   halide

2. silver halide   ——— developer ———→   elemental
                                            silver

There is neither additional silver precipitation from an external source, removal of silver, nor the formation of complex silver compounds.

The most commonly described bleaching agents are:

- potassium dichromate;
- potassium permanganate;
- potassium ferricyanide;
- mercuric chloride;
- cupric chloride; and
- cupric bromide.

The first three require the addition of a halide source, for example, sodium chloride, or potassium bromide. Other bleaching agents have also been used, such as potassium cyanide, or mercuric cyanide.

Being straightforward in theory, there are a number of pitfalls to avoid when applying such treatment in practice to photographic prints. While it is the objective of such experiments to change the density range, and therefore the contrast, of a faded, or discoloured print, the following aspects must also be considered:

1. The essential properties of the original image must be maintained:

    - grain structure;
    - resolution;
    - image tone, or hue;
    - surface properties;
    - highlight detail; and
    - physical integrity.

2. The permanence of the resultant image must be maintained or enhanced.

3. Stain formation, caused by the chemical used in the treatment, must not occur.

4. The treatment must not be damaging to the binding agent or the support.

Image stability tests permit us to satisfy one of these conditions. The occurrence of stain formation is well documented in the literature and relatively easy to ascertain. However, controlling the essential image characteristics, and the stability of the binding agent proved to be a strong challenge.

In consequence of the results of experiments described earlier, four different contemporary black-and-white prints were toned in commercially available toning solutions so as to produce silver sulfide images (15). They were then treated by five different procedures published by Pope (16), Neblette (17) and Pollakowski (18). The first two used potassium permanganate, whereas Pollakowski suggested potassium dichromate and hydrochloric acid in three different ratios. The potassium permanganate formulae both worked well, however, a highly acidic concentrated potassium dichromate solution was required to achieve the bleaching of sepia-toned prints. In the course of these experiments, one of the four print materials suffered from the formation of blisters in the emulsion and subsequent destruction of the image layer. This was a surprising observation, as the print samples were contemporary materials prepared for the experiments. Further experiments with heavily discoloured photofinishing prints dating from 1935, which

were both poorly fixed* and incompletely washed, using a potassium permanganate bleacher suggested by Sandys (19), showed a weakening of the gelatin layer during the final washing after the redeveloping step. Occasionally, the image layer was completely destroyed, leaving a faint transfer image visible on the remaining baryta layer. The large difference in pH between the bleaching solution and the highly alkaline developer was suspected to be responsible for the destruction of the gelatin.

These observations led to a study of the properties of coated gelatin layers in chemical solutions and experimental methods to evaluate and monitor its stability (20). There appears to be a relationship between the swelling of gelatin layers and their corresponding stability: excessive swelling indicates a weakening of the gelatin. Using a swellmeter described by Green and Levenson (21), the swelling and deswelling of gelatin layers on photographs was recorded as they passed through various restoration cycles. The resulting swell curves show clearly the effect of various pre-hardeners on the behaviour of gelatin layers. They also demonstrate that the final development step must be followed either by treatment in a hardening fixer, or at least by an acidic stop bath. Washing in water allows the developer-soaked gelatin to swell excessively, probably caused by an osmotic effect, and to break up completely. Thus the key steps in chemical restoration treatments, with respect to the stability of the gelatin layer, are the first two--pre-soak and prehardener--and the last step following the redevelopment; if the swelling of the gelatin beyond a threshold value can be avoided, it will survive the cycle. That the gelatin does not suffer a loss in its strength can be demonstrated by comparing its melting point (22) before and after treatment, as well as its resistance to abrasion in the wet state (23). Both tests indicate that the gelatin is not affected adversely by chemical restoration cycles; those properties of gelatin that are measured by these tests are reversible, as long as complete destruction is avoided.

In order to assess the permanence of a silver image, that has undergone chemical restoration treatments, photographic prints were subjected to accelerated aging conditions specified by the American National Standards Institute (ANSI). Specifications ANSI PH1.28-1981 (24) and PH1.41-1981 (25) suggest that incubation for 30 days at 60°C $\pm$ 2°C and 70% $\pm$ 2% relative humidity be used as an image stability test for processed black-and-white safety films. ANSI PH4.32-1980 (26) proposes to evaluate the processing of contemporary black-and-white prints by exposing them for one, ten or thirty days at 38°C $\pm$ 1°C and 94% $\pm$ 4.0% relative humidity. In all cases, samples are examined by visual inspection and density changes are measured using a densitometer.

In pursuing the kind of experimental work described here, care was taken to identify the print materials to be treated as being made by the developing-out process. As there are no published test procedures for the stability of coated collodion and albumen layers, all materials used in this work were silver gelatin prints which allowed us to monitor the properties of the binding agent. After pre-soaking in water, a hardener of the formaldehyde type containing sodium carbonate (for example, the Special Hardener SH-1 by Eastman Kodak) was shown to be most beneficial for the stability of the gelatin. Another hardener similarly effective in controlling the swelling of the gelatin is of the potassium chrome alum type. As an example, we used the formula SB-4 by Eastman Kodak. Towards the end of the treatment cycle, the re-developed print must be treated in a hardening fixer, such as Eastman Kodak's F-5 type, or the

above-mentioned SB-4. Results were evaluated by measuring density values before and after treatments. Minor density changes invariably occur. Aside from fluctuations caused by the densitometer, density losses can occur because silver halide can be dissolved by sodium sulfite in the developer, before it has been reduced to elemental silver. Loss of density in prints can also be observed as a consequence of the destruction of surface gloss (27). Yet another reason for density loss are changes in the fine structure of the image silver caused by the drying of the prints (28, 29). It is virtually impossible to subject a sample print to any kind of treatment in chemical solutions without observing minor density changes. The numerous variables in a normal treatment sequence will be discussed and recommendations will be given for specific choices.

Treatments in chemical solutions are more difficult to control when working with photographic prints than with negatives. The former are generally more delicate because of their fine grain, particular image tone, and their fragile surface properties. Of the criteria that must be observed when treating photographs in chemical solutions, the permanence of the resultant image, the avoidance of stain formation and the maintenance of the stability of gelatin, can be met. Maintaining the characteristics of the original image is by far the most important requirement. These properties are essentially determined by the size, structure and distribution of the image silver. Its fine structure can be studied--and possibly controlled--with the aid of an electron microscope. Future efforts will be directed in this laboratory towards an understanding of the effect of bleach and redevelopment procedures on the morphology of image silver and the corresponding image properties.

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ANALYSE DE QUELQUES CODEX MEXICAINS CONSERVES A LA
LA BIBLIOTHEQUE NATIONALE DE PARIS

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RESUME

Les codex mexicains conservés à la Bibliothèque Natio-
nale de Paris sont décrits dans deux catalogues établis
à la fin du siècle dernier. Les fibres d'Agave sont
mentionnées comme constituant du support de la totalité
des manuscrits écrits sur écorce.

L'analyse micrographique de 22 codex a montré qu'il ne
s'agissait pas de fibres d'Agave mais de moracées.

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Les recherches effectuées sur les supports des docu-
ments anciens présentent un intérêt historique et
géographique. L'étude d'une collection de documents
provenant d'un même pays ou d'une même période permet
une connaissance plus approfondie des habitudes, des
techniques et de la civilisation de ceux-ci.

La Bibliothèque Nationale de Paris conserve plus de
400 codex mexicains dont certains datent de la civi-
lisation précolombienne. Il nous a donc paru intéres-
sant, en accord avec le Conservateur du Département
des Manuscrits Orientaux, d'essayer de déterminer la
nature et la provenance des plantes ayant servi de
base aux supports de ces codex.

DEFINITION DU CODEX

Les codex sont des testaments documentaires relatifs
aux peuples de l'Ancien Mexique (1,7). On distingue :

1. Les codex préhispaniques : il en reste à l'heure
actuelle 21 ou 23. Ce sont des manuscrits avec des
pictographies idéographiques peints en couleurs conven-
tionnelles de signification déterminée. Ils sont écrits
sur "papier"*indigène, sur peau de cerf ou de jaguar
ou sur tissu de coton. Ils sont formés de larges bandes
pliées en forme de paravent, écrits des deux côtés et
protégés aux extrémités par des couvertures de bois.

2. Les codex posthispaniques : ce sont aussi des manus-
crits pictographiques avec, en plus, des textes en
langue indigène ou   espagnole. Ce sont, soit des co-
pies de codex disparus, soit des manuscrits originaux
écrits sur feuilles ou bandes de "papier" indigène
ou européen (espagnol ou italien).

FABRICATION DU SUPPORT

1. Matières premières utilisées :

   1.1. *"Papier"* (13) : il était fait à partir du paren-
chyme et des parties libériennes des plantes suivantes :

- Feuilles de Metl ou maguey (*Agave americana*); dans
toutes ses espèces et variétés : Henequen (*Agave
Fourcroydes Lem.*), Zapupe (*Agave Deweyana Trel*), etc

* Le terme papier est utilisé improprement, car il
désigne ici une écorce ou une feuille battue et non
un feutrage artificiel de fibres.

- Ecorces de quelques moracées ou amatl. : caoutchouc
(*Castilloa elastica Cer.*), amate de terre froide (*Ficus
nimphaefolia L.*), amate de terre chaude (*Ficus bomplan-
dia Miq.*), etc .)

- Fibres de Thalles : de yezotl ou izote du genre yuca

   1.2. *Peau* : de cerf ou de jaguar tannée

   1.3. *Tissu ou couverture de coton*

Des analyses microscopiques et chimiques ont montré que
la matière première correspondait avec le lieu d'origi-
ne des codex. Ainsi, en terre froides, on employait les
feuilles de maguey, en région tempérée, l'écorce d'Izote,
le tezoyatl et le zoyamatl et en terres chaudes, les
racines et les écorces d'amate.

2. Méthodes de fabrication des supports d'origine végé-
   tale :

La fabrication est la même qu'il s'agisse de feuilles
d'Agave ou d'écorce de mûrier.

On connaît peu de détails sur la technique précolombien-
ne. Les seuls écrits sur ce sujet sont bien postérieurs
à la Conquête, mais des peuples indigènes ont gardé, par
tradition orale, des méthodes anciennes dont voici les
principes :

- Les feuilles d'Agave sont récoltées et mises à pour-
rir dans les ruisseaux ; le fil est alors lavé et uti-
lisé.

- Les feuilles de moracées se trouvent accollées à
l'écorce de l'arbre. Pour les obtenir, on fait une cou-
pure transversale dans le tronc près d'une ramure encore
tendre ; on tire les fibres et l'écorce en essayant
d'arracher un morceau le plus épais et le plus long pos-
sible. Les fibres sont ensuite détachées de l'écorce
avec les doigts et déposées dans l'eau courante pour
faire sortir les matières colorantes ; elles sont alors
tapées avec un battoir de bois ou avec une pierre jus-
qu'à ce qu'elles soient très molles ; on les étend en-
fin sur des planches ou des pierres lisses pour les
frapper doucement avec une pierre présentant des rainu-
res ou des stries, afin d'emmêler les fibres. Le
"papier" sec présente une surface lisse (côté planche)
et rugueuse (côté pierre). Les imperfections du côté
rugueux obligeaient les utilisateurs à le recouvrir
d'une couche laiteuse d'origine végétale ou minérale
pour permettre l'écriture.

ANALYSE DES SUPPORTS DES CODEX CONSERVES A LA BIBLIOTHE-
QUE NATIONALE DE PARIS

1. Choix des manuscrits (annexe)

Les codex de la Bibliothèque Nationale de Paris sont
conservés au Département des Manuscrits Orientaux. Ils
sont disposés dans des boîtes ; certains, plus fragiles,
sont montés sous plexiglas. Les plus anciens ne sont
plus communiqués.

Parmi les manuscrits que nous avons pu consulter, nous
avons opté pour ceux dont le support nous a paru le plus
caractéristique et sur lesquels le prélèvement était
possible. Nous avons également choisi deux papiers
d'origine européenne pour vérifier leur composition.

2. Méthodes d'analyse

Quelques fibres ont été prélevées à la surface des sup-
ports. Elles ont été dispersées dans une goutte de
réactif de Hezberg ou chloroiodure de zinc sur une lame
de verre et observées au microscope. Ce réactif colore
en rouge vineux les fibres cellulosiques provenant
d'écorces végétales, en bleu foncé, celles issues du
bois et, en bleu clair, les substances pectiques.

Les fibres d'Agave sont fusiformes, assez courtes, colo-
rées en bleu foncé. Par contre, les fibres de moracées
sont beaucoup plus larges, plus longues, fragmentées en
tronçons, avec une paroi épaisse comportant des plis de
flexion. Ces fibres se colorent en rouge vineux et,

de plus, présentent comme particularité, une membrane extérieure fine pectocellulosique colorable en bleu clair que l'on appelle la "chemise".

3. Résultats (voir photos) :

Les deux papiers d'origine européenne, étaient composés de chiffons de lin. Par contre, toutes les fibres prélevées sur les papiers d'écorce, quel que soit l'aspect du support fin ou épais, clair ou coloré, doux ou rugueux, ont présenté les caractéristiques des moracées. Certaines étaient entières et très belles, d'autres, coupées ou usées, leur "chemise", qui était très déchirée, n'adhérait plus à la fibre. Ceci peut être dû à un travail plus intensif des fibres au moment de la fabrication ou à une usure provenant du vieillissement. L'âge et la nature de la plante peuvent également jouer sur les dimensions des fibres.

CONCLUSION

Cette étude nous a permis de montrer l'importance de l'apport de la science dans la connaissance des oeuvres d'art.

A la fin du siècle dernier, OMONT et BOBAN ont élaboré deux catalogues où ils décrivaient tous les codex mexicains conservés à la Bibliothèque Nationale de Paris. D'après l'aspect des documents, ils ont pensé que les supports étaient constitués de fibres d'Agave mexicana.

Les analyses microscopiques effectuées au laboratoire sur les supports de 22 codex sur écorce ont montré qu'il ne s'agissait pas de fibres d'Agave, mais de moracées ou amatl. Par contre, les fibres ayant un aspect morphologique semblable, nous n'avons pas pu déterminer de quelle espèce de moracée il s'agissait.

De nombreux auteurs ayant prouvé que les écorces de moracées étaient utilisées pour la fabrication du "papier" dans les régions chaudes, on pourrait peut-être déduire de ces analyses que les codex étudiés proviennent de ces régions.

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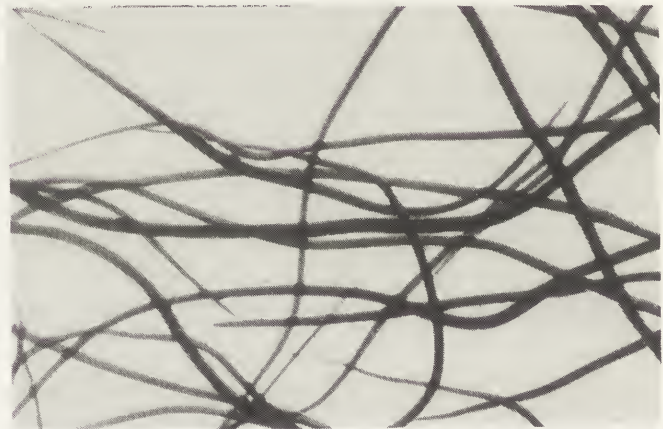
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(15) VAN HAGEN (Victor).- *Paper and civilisation*, The Scientific monthly October 1943, vol. LVII, p. 301-314

(16) VINDEL (Francisco).- *En papel de fabricacion azteca fue impreso el primo libro en America*, Madrid, 1956
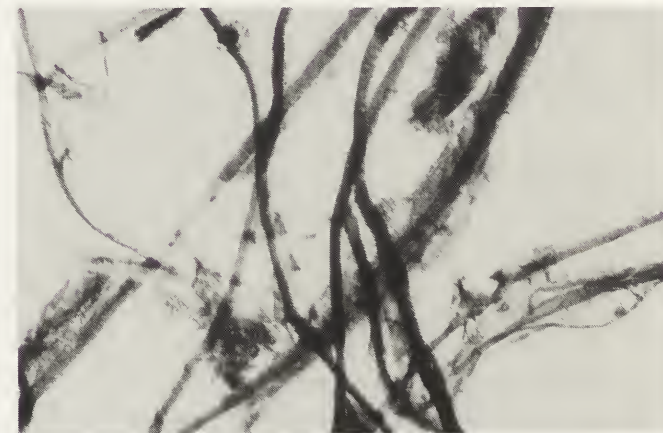
Fibres d'Agave mexicana. G = 320x
Elles sont fusiformes à pointe effilée et opaques.

Codex 390. G = 320x

Les fibres de moracée présentent des parties claires et foncées. Dans les zones foncées, la fibre est intacte et comporte sa chemise, alors que, dans les zones claires, celle-ci est déchirée ; on voit alors apparaître des plis de flexion. Les parties nuageuses qui se trouvent autour de quelques fibres sont constituées par des lambeaux de chemise déchirés et gonflés dans le réactif.

LISTE DESCRIPTIVE DES CODEX ETUDIES

Cote	Titre *	Description *	Aspect du support
1-10	Histoire de la nation chichimèque (Xoloth)	Manuscrit composé de 10 planches - original sur papier indigène d'Agave mexicana	Papier épais, très brun, rugueux
13-14	Mappe de Tepechpan (1298-1596)	Manuscrit figuratif, original sur papier indigène d'Agave mexicana	Papier très épais, clair, très rugueux
15-17	Le codex en croix	Manuscrit figuratif composé de 18 feuilles, original sur papier indigène d'Agave mexicana	Papier épais, brun, très rugueux
18-19	Le tonalamatl	Calendrier religieux et divinatoire	Papier très épais, très brun, très rugueux
22	Manuscrit de 1528	Annales historiques de la nation mexicaine	Papier épais, brun rugueux
23-24	Codex mexicanus	Manuscrit figuratif Original sur papier indigène d'Agave mexicana	Papier assez épais brun clair, très lisse
26	Cedula de diligencia	Manuscrit figuratif Original sur papier indigène d'Agave mexicana	Papier très doux, foncé, très mou
27	Contrat de commande-rie 17 octobre 1554	Original sur papier européen	
28	Contributions ou tributs	Manuscrit figuratif Original sur papier d'Agave mexicana	Papier assez épais, très doux
29	Pièce justificative d'un procès (Mexico, 13 octobre 1571)	Manuscrit figuratif Original sur papier d'Agave mexicana 15 feuillets	Papier épais, beige assez lisse
30	Reçus (Pliego de recibos) 1564	Manuscrit figuratif Original sur papier d'Agave mexicana - 13 feuillets	Papier assez épais, beige, lisse et doux
46-58	Histoire tolteco chichimèque	3 fragments - 59 pages, papier euro-péen dans une cou-verture indigène	Papier vergé fin, couverture brun rugueux
81	Fragment d'histoire chichimèque	Manuscrit figuratif Original sur papier indigène d'Agave mexicana	Papier très épais, brun, très rugueux
82	Titre de propriété	Manuscrit figuratif Original sur papier d'Agave mexicana	Papier fin, vergé, souple, très doux
83	Codex mexicanus	Manuscrit figuratif Original sur papier d'Agave mexicana	Papier très fin, abîmé, brun clair, très rugueux
110	Pièces d'un procès (1590)	Manuscrit figuratif Original sur papier indigène d'Agave mexicana	Papier fin, très brun, très souple, abîmé
111	Pièces d'un procès (1566)	Manuscrits figuratifs Originaux sur papier d'Agave mexicana	Papier fin, beige clair
114	Titre de propriété	Manuscrit figuratif Original sur papier d'Agave mexicana	Papier très brun, très rugueux
375	Mappe Baur-Goupil	Manuscrit figuratif sur Agave mexicana	Papier très doux, beige, souple et mou
386	Codex peresianus (Maya)	Manuscrit figuratif sur papier d'Agave mexicana	
390	Rôle des impôts perçus sur les habitants de Tlatengo en 1562	Manuscrit figuratif sur Agave mexicana	Papier très rugueux brun clair, très épais

Cote	Titre	Description	Aspect du support
393	Registre d'une paroisse	Manuscrit en langue nahuatl sur papier d'Agave mexicana	Papier fin, clair, souple, très doux, grandes traînées longitudinales
394	Trois pièces d'un procès (1530)	Manuscrit en langue espagnole sur papier d'Agave mexicana	Papier beige clair, souple
401	Mapa antiguo de los terrenos del pueblo de San Simon Calpul-alpalm	Manuscrit figuratif composé de 6 feuillets écrits recto-verso en langue nahuatl sur Agave mexicana	Papier épais, brun, grossier

* D'après le Catalogue des manuscrits mexicains XIII-1
       Codex mexicains - catalogue XIII-3

MICROBIAL RESISTANCE OF BOOK PAPER

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SUMMARY

A differential approach to the choice of substances providing microbial resistance of paper and books is grounded. Principal requirements to biocides are formulated. Here are presented biocides recognized at present to be the most suitable for paper conservation during the paper pulp restoration process and for treatment of used paper and adhesives. Barrier protection of books exposed to the danger of fungal deterioration by means of biocidal fibers is proposed. Comparative efficacy of methyl-p-oxybenzoate, p-dioxydiphenyl methane, polyhexamethylene guanidane, alkylbenzil-dimethyl ammonium chloride against fungi is given. Biocidal properties of these compounds due to the effect of ultra-violet radiation, enhanced temperature and running water is investigated. Positive and negative properties of the biocides used for book conservation are revealed. Advantages of polymeric biocidal compounds over monomeric ones are found. Barrier book protection by polyacrylonitrile fibers modified with quaternary ammonium compounds is described.

Introduction

Biological deterioration of anthropogenic substrates is being expanded everywhere. This provdes unfavorable conditi ons for book conservation. The probability of biological deterioration of books grows and interest to the problem of their microbial resistance is maintained. The requirements which biocides must meet for book protection are as follows.
1. Combined effect covering all biological factors capable of book damage.
2. Ability to inhibit spore germination and fermentive activity of organisms.
3. Favorable action of biocides and their decay products on the permanence and durability of paper.
4. Minimum toxicity of compounds and metabolites for warm-blooded animals: limit concentration, 1-2%. Absence of carcinogenic and teratogenic properties and of environmental pollution.
5. pH-level close to neutral or with shift towards alkalinity.
6. Moisture adsorption not higher than that of protected materials.
7. Compatibility and uniform distribution in the material.
8. Chemical interaction with book materials without loss of efficacy.
9. Solubility in water, ethyl alcohol. Possibility to dispense with other organic solvents.
10. Colorlessness of compounds and their decay products.
None of the known compounds meets all of the requirements above. Therefore, recommendations for paper protection against biological damage are not stable and are regularly altered. In addition, there occurs adaptation in time of organisms to substances which have been in use. Gradually, more is learned about each biocide. In due course, not only positive, but also their negative properties are revealed. Therefore, the search for new biocides continues.
Book protection against biological damage can be provided using various methods for different modes of conservation. Selection of suitable biocides for this purpose is the main task. Chemical compounds come in contact with paper and print and their further destiny takes shape jointly.

Investigation results of book protection methods

Protection in paper making process. Over 20 preparations of different chemical constitution are known to be in use for this purpose. They are substituted phenols, organo-mercuric and organo-tin compounds, phenol and quinoline derivatives, dithiocarbamates, and other compounds.
Inclusion of biocides during the paper pulp restoration process has only recently come into being. Earlier, pentachlorphenol, salicyl anilid and 8-hydroxyquinoline were used for this purpose.   A successful experience was protection using latex of tributiltinmetacrylic resins. The latex was included in the paper pulp in the following concentrations: 2%, 1%, 0.5%, 0.25%, 0.125%. pH-level was always equal 5.7. Experimental paper had a mass of 40 g per square metre. The samples were applied to the surface of agar solution medium and inoculated with two-weeks spore suspension of Aspergillus terreus Thom. The spore suspension prepared on Czapek's solution medium was applied to the centre of a paper sample. Inoculum revival and colonial growth were watched. Dependence of colonial diameter on latex concentration is presented in Fig. 1.
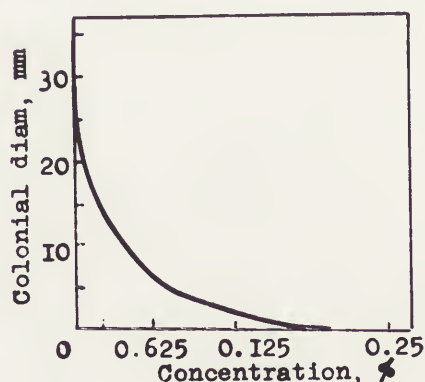

Fig. 1. Inhibition of colonial growth of fungi by latex of tributoxy-tin acrilic resin.

It can be seen that 1% latex content provides conservation during the paper pulp restoration process. In addition, latex improves the mechanical properties of paper. The folding endurance of paper at 0.5-1% latex content in dry weight of fibers increases by 40-60%. Latex does not change the external appearance of paper. It is assumed that the peculiar mechanism of biological efficacy inherent in the latex of tributyl-tin copolymers results in their low toxicity for men.
        Toxic fragments of trialcyltin split off for increased humidity and enhanced biological deterioration. This is the process which provides protection. At the same time, tributyl-tin copolymer molecules present no serious danger to environment.
Processing of used book paper. Protection of adhesives. Use of antibiodeterioration compounds for this purpose is practised at paper conservation departments. These preparations

in such cases must meet stringent require -
ments.
We have carried out a comprehensive investi-
gation of several chemical compounds which
are widely spread in conservation and have co
considered not only their biocidal properties,
but also their resistance to the effect of en
vironmental factors.
Antifungal properties were evaluated using
the following fungi which enhance paper de-
terioration: Aspergillus terreus Thom, Trich-
oderma viride Pers. ex Fr., chartomium globo-
sum Kunze ex Fr. The paper was impregnated
with solutions dilution ratios of 4 to 0.25%.
After drying, a suspension of fungal spores
was applied to samples and incubated for 48
hours. Afterwards, the samples were placed on
brevery-wort-agar in petri dishes. Inception
and fungus colonial growth were observed.
Colony diameter in mm was measured. Dependen-
ces between the rate of colonial growth and
antifungal substance concentration were de-
rived. They were found also for samples ex-
posed to the following three kinds of envi-
ronmental factors.
1. Irradiation using a mercury vapour lamp
during 10 h at an illumination intensity of
10,000 1x.
2. Heating ar a temperature of $100\pm2^{o}C$ during
72 h.
3. Washing in running water during 24 h.
Retention of antifungal properties due to
these factors was defined for several sub-
stances often used in practice.
Methyl-p-oxybenzoate - a substance soluble in
ethyl alcohol. A well-known conservant of var-
ious materials. Provides paper protection in
concentrations not less than 1.5-2%. Has suf-
ficient resistance (Fig. 2) to the effect of
temperature and ultra-violet radiation. Rea-
dily moves away. Protects moreefficiently
proteinstarch composition. For 1.5% content
of methyl-p-oxybenzoate, the antifungal pro-
perties were conserved at 100% relative air
humidity during 6.5 months, with initial pH-
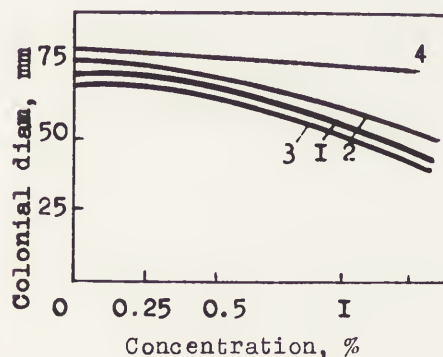-level varying from 5.5 to 7.

Fig. 2.
Inhibition
of colonial
growth of
fungi by
methyl-p-
oxybenzoa-
te.
I - con-
trol, 2 -
temperature,
3 - ultra-
-violet ra-
diation,
4 - water.

p-Dioxydiphenyl methane provides safe paper
protection in 1-0.6% concentration.   The
effect of high temperature somewhat reduces
its protective action and ultra-violet radia-
tion ultimately even improves biocidal effi-
cacy. For prolonged action of running water
the antifungal substance is washed-out, which
results in loss of protective properties
(Fig. 3). The substance is readily distribu-
ted on the fiber surface. This was established
by microscopic investigation. Fungicidal ac-
tion of p-dioxydiphenyl methane was also re-
vealed.
Polyhexamethylene guanidine adds biological
resistance to paper in a concentration of
0.5-1% .   This substance offers good re-
sistance to the effect of ultraviolet radia-
tion and reduces activity under the influence
of the temperature factor (Fig. 4). Protein-
starch compostitions with 1.5% of the sub-
stance remained unchanged at 100% relative
air humidity during 2.5 years without losing

their properties. The substance is concen-
trated in deteriorated parts of fibers pro-
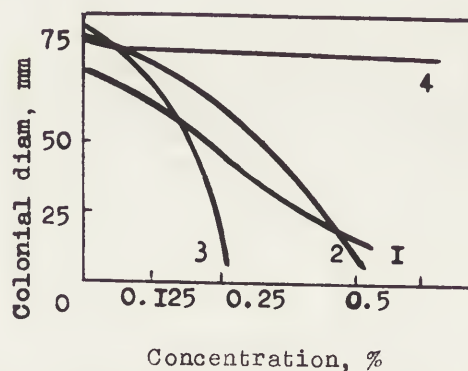tecting them against fungal celluloses. In

Concentration, %

Fig. 3. Inhibition of colonial growth of
fungi by p-dioxydiphenyl methane.
1 - control, 2 - temperature, 3 - ultra-vio-
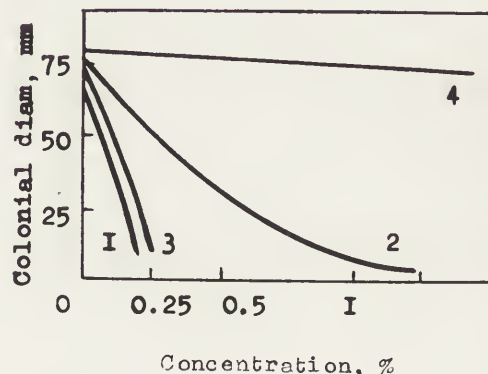let radiation, 4 - water.

Concentration, %

Fig. 4. Inhibition of colonial growth of
fungi by polyhexamethylene guanidine.
1 - control, 2 - temperature, 3 - ultra-vio-
let radiation, 4 - water.

contact with polyhexamethylene guanidine tre-
ated paper, fungal spores do not germinate
and partially perish. Quaternary ammonium
compounds - widespread biocides in the resto-
ration practice .   Satisfactory paper
protection is obtained with 0,5-1% alkylben-
zildimethylammonium chloride .   The sub-
stance is resistant to ultraviolet radiation
and temperature, but is exposed to washing-
out. (Fig. 5). The preparation is notable for
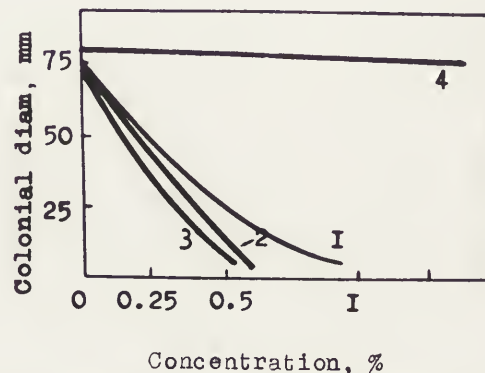a wide specrum of fungal action.

Concentration, %

Fig. 5. Inhibition of colonial growth of
fungi by alkylbenzildimethylammonium chlori-
de.
1 - control, 2 - temperature, 3 - ultra-vio-
let radiation, 4 - water.

Quaternary ammonium compounds on the whole, however, must be used with care. They may reveal incompatibility with anion surfac - tants, with soaps, anion dyes, with halogen substances, silicons, carboxymethyl cellulo- se, and others. They reduce their activity in the presence of calcium, magnesium, allumi- nium, iron and promote cellulose swelling of fibers.

Thus, the least negative properties are in- herent in polymeric compounds, p-dioxydiphe- nyl methane and polyhexamethylene guanidine which protect paper in the microconstitution and are therefore the most effective.

Indirect preservation of books using barrier materials. Chemical compounds included in the composition of the book may change its components. Therefore, attention was paid to materials which can be used by bringing them in contact with the book. Satisfactory resu- lts were obtained with fibers having bioci- dal properties and, in particular, with poly- acrylonitrile fibers modified with quaternary ammonium compounds. Negative properties of the latter, in this case, were not revealed. In addition fiber as spacing material can at any time be removed from the book.

Inclusion of biocide in the spine and cover of the book is the most important in book preservation. Biocidal fiber can be conveni- ently inserted and readily removed from the book chemical and mechanical treatment. The testing of polyacrylonitrile fibers modi- fied with quaternary ammonium compounds revealed high biocidal ability which manifes- ts itself quite clearly when in contact with fungal spores. The latter lose their germi- nation ability which is not restored after the fibers are removed. Inhibition of the colonial growth of fungi in the presence of the above fibers is illustrated in Fig. 6. Data are given for fibers modified with al- cyltrimethylammonium chloride compared with control polyacrylonitrile fibers. A high de- gree of inhibition of the colonial growth is established.

Books of the 18th-19th centuries interleaved with these fibers remained undamaged during one year although the relative air humidity during the most part of the term persisted at 90-95%. There is reason to believe that the future belongs to such indirect preserva- tion methods.

Inclusion of latexes of tributoxy-tin-acrilic resins to protect paper during its production and the paper pulp restoration process. Gua- nidine and p-dioxydiphenylme thane derivatives to treat used paper. Polyhexamethylene guani- dine, methyl-p-oxybenzoate, formaldehyde to preserve the adhesive. Polyacrylonitrile fi- bers modified with quaternary ammonium com- pounds are proposed as barrier materials for book protection.
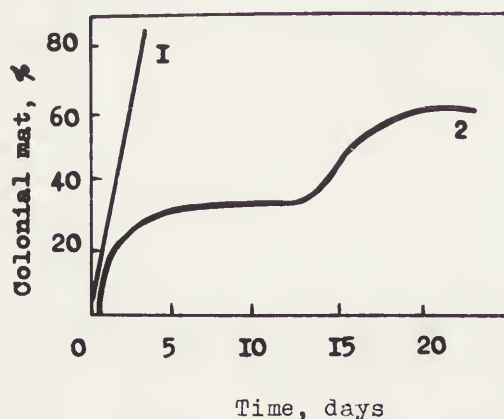

Fig. 6. Inhibition of colonial growth of fungi by biocidal polyacrylonitrile fibers. 1 - control, 2 - biocidal fibers.

Conclusion

Methods of book preservation against bio- deterioration are being currently developed. Concrete recommendations, therefore, are of temporal value. Recent investigations per- formed at the M. E. Saltykov-Shchedrin State Public Library suggest the following methods of paper and book preservation.

EVALUATION OF CONSERVATION PROCESSES EFFECT ON DURABILITY OF RESTORED MATERIALS

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SUMMARY

The author shows the possibility to evaluate the conservation processes effect on durability of the materials restored on the basis of their strength time relationships. As an example experimental data are described on the effect of bleaching and transparency removal on time relationship of the parchment strength.

One of the most complicated tasks of modern investigation in the field of cultural and historical monuments conservation is evaluation of their durability, that is of the time of their existence before they begin to disintegrate after some conserving operations. Usually, when defining the possibility to utilize new compositions and methods, a number of physical-mechanic and physical-chemical properties of the material conserved are defined and compared before and after the treatment. If these properties are found satisfactory an accelerated luminous, thermal or complex thermal-luminous ageing is carried out to evaluate the state and preservation of the material in future.

In case of thermal ageing durability prediction is based on the Arrenius equation: temperature increase by $10^{\circ}C$ is believed to accelerate the ageing process three times. In case of luminous ageing the durability forecast is based on the correlation of physical-mechanic and physical-chemical properties after thermal and luminous ageing.

Accelerated ageing, however, gives only a vague idea of durability as it does not always correspond to the natural ageing process. Besides, durability is evaluated primarily on the basis of the material strength characteristics, e.g. breaking or bending strength

which is defined either under constant loading speed (breaking) or under periodical cycling loading (bending). However, the characteristics obtained in such loading conditions do not take time factor into direct account.

Meanwhile, in case of strength testing under constant loading conducted for a wide range of materials (such as metals, plastics, polymer fibres, paper, finely dispersed porous bodies, etc.) there exists a direct relationship between durability and the load applied. This relationship is described by the following exponential equation:

$$\tau = A e^{-\alpha \sigma}$$

τ - being the time before disintegration;
σ - a given stretching load;
e - natural logarithm base;
A, α - constants.

It is obvious from the above given equation that the logarithm of the time before disintegration is linear with the load applied and may be graphically expressed as a straight line:

$$lg\,\tau = lg\,A - \alpha \sigma\, lg\,e \qquad \text{or}$$
$$lg\,\tau = B + C\sigma$$

$B = lg\,A, \quad C = -\alpha\,lg\,e$ - being constants.

When carrying out practical investigations in the field of conservation, time relationships are used to predict durability of paper. But time relationships for strength may evidently as well be a reliable criterion of harmless application of almost every method and material in the conservation process. Indeed, if we obtain time relationships for some object's strength (such as paper or any other) before and after some conserving operation, we may exactly define by the straight lines relative position whether the operation mentioned decreases the object's durability time. Moreover, unlike the durability prediction no assumptions are necessary. For example, we do not take into consideration the effect of loads in storage which may not exist at all in reality.

The paper presented deals with experimental investigation of the problem whether it is possible to evaluate the effect of conservation processes on durability of restored materials on the basis of time relationships for strength. The concrete case deals

with the effect of two processes on parch-
ment durability - removal of pigment stains
with Chloramine B and removal of transparen-
cy by stretching.

Time relationships for strength were obtain-
ed with the help of an ordinary tearing ma-
chine. As the machine allows to pre-define
the load applied but does not fix the moment
of breaking of the samples, the determina-
tion of long-term strength (i.e. of every
experimental point on the $\lg \tau$ direct line
as a σ function) was conducted by way of
selecting the minimum load under which the
samples' disintegration happened during a
certain pre-defined period of time. To ob-
tain reliable results when defining every
value of long-term strength, not less than
I5 to 20 samples were tested.

The onjects of investigation were a new
parchment of Soviet production and an old
binding parchment. Removal of pigment stains
was imitated by way of treating the parch-
ment with 6-IO per cent Chloramine B aqueous
solution. The total treatment duration was
5 hours. Transparent samples were obtained
as a result of intense watering and subse-
quent drying-out of the parchments in a
press under strong load. Transparency remo-
val was reached by slight stretching of pre-
watered samples.

Earlier, when developing the two methods,
the effect of Chloramine and stretching on
parchments was determined by way of measu-
ring their breaking strength, elasticity
(against extension) and the aqueous extract
pH value both immediately after the treat-
ment and after accelerated ageing in ultra-
violet radiation. On the basis of the re-
sults obtained (Tables I and 2) we assumed
that neither of the two processes effected
the parchment durability.

However, the determination of time relati-
onships did not totally confirm this assump-
tion. It appeared that the pre-disintegra-
tion time decreased after Chloramine B
treatment under any given load (Fig. IO),
that is the treatment was accompanied by
durability decrease and was not harmless.
Then the removal of pigment stains with
Chloramine was possible only in case of
emergency.

Table I. CHLORAMINE B EFFECT ON THE PARCH-
MENT PROPERTIES

Group of samples	Strength (kgs/mm^2)	Relative lengthe-ning (per cent)	pH
Before bleaching	3.4	IO.0	7.2
After bleaching	3.5	7.7	7.I
Before bleaching after ageing	4.2	7.3	7.2
After bleaching and ageing	3.6	7.5	7.2

Table 2. STRETCHING EFFECT ON THE PARCHMENT
PROPERTIES IN CASE OF TRANSPARENCY
REMOVAL

Group of samples	Strength (kgs/mm^2)	Relative lengthening (per cent)
Before stretching	7.7	26.2
After stretching	8.I	25.0

And on the contrary, stretching of samples
leading to considerable decrease of transpa-
rency does not effect the strength time re-
lationship (Fig. 2). This means there is no
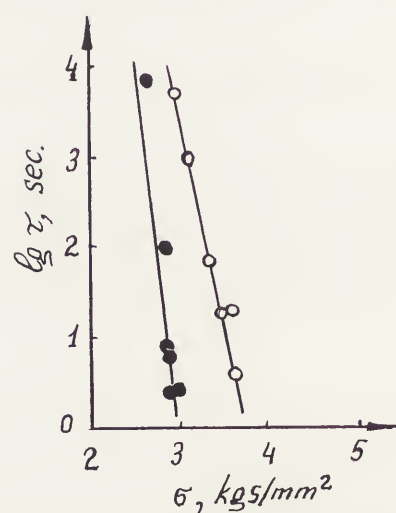durability decrease and this method of trans-
parency removal is harmless.

Fig. I. Time relationship for the parchment
strength before and after the Chlo-
ramine treatment (o - before and
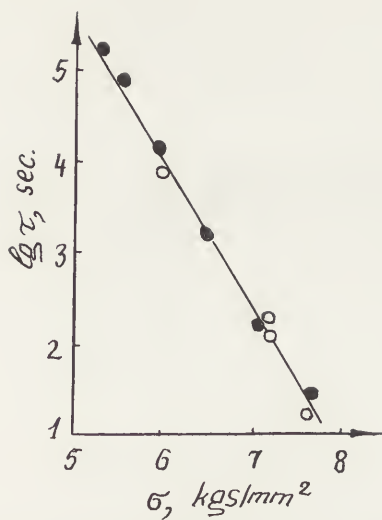● - after the treatment)

Fig. 2. Time relationship of the parchment
        strength before and after stretching
        (○ - before and   ● - after stret-
        ching)

The analysis of the results shows that, in-
deed, the strength time relationships allow
to obtain reliable information about the
effect of conservation methods and reagents
used on durability of the restored material.
Due to this the determination of time rela-
tionships should obviously be used by the
investigators in the field of conservation.

Section 15

Mural Paintings and Mosaics

Peintures murales et mosaïques

CONSIDERATIONS REGARDING THE STATE OF
CONSERVATION OF DA VINCI'S 'LAST SUPPER'
BEFORE STARTING RESTORATION OPERATIONS

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SUMMARY

The restoration of Leonardo's painting in the
Refectory of the Convent at Santa Maria delle
Grazie began in 1978. The following
communication analyses in its different
aspects the state of conservation and the
pertinent restoration program.

The subjects specified in detail are the
following:

The State of Conservation of the Chromatic
Surface

Dust and Dirt

Microflora

Stucco Work

Anchoring Materials

Superimposed Restoration Work

All the scientific researches connected with
the restoration work carried out by
different departments of Milan High Tecnology
School, are coordinated by Olivetti Cultural
Department as relevant part of its financial
and organization support to the whole
restoration project.

INTRODUCTION

The 'Last Supper', which was painted by
Leonardo da Vinci on the north wall of the
Refectory of the convent of Santa Maria delle
Grazie in Milan, has been subjected to severe
restorations over the ages.

The first considerations start with Lomazzo,
who attributed the painting's deterioration to
the use of "oil painting", instead of the
traditional "good fresco", and to the use of
the wrong type of primer base. Vansani also
criticized the use of "bad technique". It was
not until the 17th century that environmental
phenomena were blamed for the deterioration of
Leonardo's work. These conditions, including
the humidity in the air, caused, in fact, the
forming of a condensate on the chromatic
surface of the painting, causing it to
'whiten'.

Numerous reports have been written regarding
the condition of the refectory walls,
including the lunettes at the top, which state
the different hypotheses regarding Leonardo's
technique and the various restorations
undertaken.

The problem is still an open one and, today,
studies regarding the 'Last Supper' continue
to be carried out.

The State of Conservation of the Chromatic
Surface

At first glance, not much of the detail in the
painting is definable because of its hazy
appearance and because of its having become
darkened over most of its surface. There are
pock marks, wrinkles, dust and mold on the
surface, while the thin, tormented remains of
the original color - as well as the holes -
are covered with altered restoration work.

A close-up examination of the work reveals
that there are two general areas of
consideration:

a) the material covering the original surface

b) the deterioration characteristics of the
original paint materials

As regards the first consideration, a, we
have the following:

Dust and Dirt - There is a superficial layer
of dust covering the painting and is of recent
deposition. Examination under the microscope
further reveals the presence of small
globular masses which are typical of the
particles found in smog.
Beneath this layer there is a thicker layer
of dirt, which is the accumulation of ages
and which has been consolidated by anchoring
operations conducted in the past.
Dark deposits are found in the centers of the
concave parts of the shell-shaped scales, as
well as infiltrated down deep into the
craquelures and on the upper edges of the
areas where the original color confines with
the holes.

Microflora - A small amount of microflora can
be seen with the naked eye. Microscopic
examination shows the aggressive action of the
mycelial hyphae, a tangle of grayish-white and
greenish filaments in a bushy-like structure.

Stucco Work - There are numerous points, all
over the painting, where stucco has been
applied. In some places it even covers the
original color. As many as five different-
colored stucco materials, black, red, gray,
brown and white, have been found in super-
imposed layers.

Anchoring Materials - The whole chromatic
surface of the painting is glossy, due to the
lacquer-like substance which covers it. This
layer is very thin and was applied on occasion
of the last restoration. The layer is thicker
in the concave parts of the shell-shaped
scales and in the hole areas.
There are some areas which are full of wax,
the wax probably having been applied to fill
in the spaces lacking in color, as well as to
provide further anchoring.

Superimposed Restoration Work - An initial
examination of the painting showed chromatic
alterations in all areas, the colors being
considerably different from the original.
These areas which are different completely
cover Leonardo's colors and reflect the
artistic tastes of the particular periods
when the restorations were made. The first
two restorations were out-and-out repaintings.
Later on, at the beginning of the 19th
century, more conservative consolidations
were attempted.

1726 - M. Bellotti completely repaints the
surface and applies a final coating of
an oil-base lacquer.

1770 - G. Mazza scrapes away Bellotti's
restoration work, uses a 'detergent' to

clean the surface, then reintegrates
up to the last 3 figures on the left.

1819/53 - S. Barezzi makes two interventions,
attempting a 'strip-off' operation but,
having failed in this first attempt,
uses a strong glue to reattach the
particules of color that have been
pulled outwards.

1904/08 - G. Caveneghi treats the surface
with a 'mastic material, diluted in
appropriate substances, which would be
least affected by the hygrometric
conditions'.

1924 - O. Silvestri follows Barezzi with
another anchoring attempt, using
diluted mastic material and going over
the surface with a hot iron roller.

1947/54 - M. Pellicioli removes some of the
repainted portions and reconsolidates
the painting with rubber lacquer
thinned with alcohol.

As regards the second consideration, b, we
have found the following:

Lifted Particles - This is the most severe
'malady' afflicting the painting. There are
many small particles of paint which have
lifted up, due to the lack of adhesion and
cohesion in the various preparatory layers,
and have caused the formation of fragile
scales or flakes.

Scale Shifting and Breakage - A close-up
examination of the chromatic surface shows
that the scales and bits of original color
have shifted from one point on the painting
to another. This phenomenon is the result
consolidation operations conducted in the
past, whereby spatulas and various other
types of instruments were used in an attempt
to make the paint adhere better to the under-
lying support layers.

Flake Abrasion - The attempts made to try to
make the paint adhere better to the under-
lying layers caused the edges of the lifted
scales to be worn or abraded. The damage is
quite noticeable because of the exposure of a
white substance used in making the under-
lying support surface for the paint.

THE STABILIZATION OF A ROMAN MOSAIC AS A
PANEL PAINTING

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SUMMARY

In the course of excavations carried out in
1961-63 and then again in 1982, remnants of
a late Roman building and some mosaic
fragments - among others a four-colour
mosaic of geometrical pattern /25ox9o/ -
were found near Nagyharsány, in the south
of Hungary.

At the request of the excavation leader,
Ferenc Fülep the mosaic was lifted in situ
for the purposes of stabilization and
presentation as a panel painting.

Three layers of gauze were stuck onto the
mosaic by an emulsion called Budaplast. The
surface thus stabilized was cut off from
the terrazzo embedment by a thin woodfibre
panel pushed in between step by step. The
terrazzo remains on the back of the mosaic
were removed in the laboratory. Smaller
gaps were filled epoxy resin made
thixotropic by asbestos wool and aerosil.
Afterwards the backside of the mosaic was
covered by two layers of glass-wool,
impregnated by epoxy resin.

An aluminium frame of appropriate Tee-
sections /21ox7o cm in size/ was then stuck
onto this surface together with stifferers
of the same size in the longitudinal and
lateral axis. In the cross direction 4 mm,
hard aluminium wires were fixed in parallel
every 8 cm. By lapping them over the frame
was stuck onto the back of the mosaic by
further two thin layers of epoxy resin and
glass wool. Thus the surface of the mosaic
and the aluminium frame is attached to each
other by the 3-4 mm thick epoxy resin
adhesive.

Turning over the mosaic consolidated in this
manner, the temporary gauze layer was
removed. The surface was cleaned and the
missing tesserae of the mosaic were
completed by epoxy resin /Eporezit R-3 and
FM-2o/ following the repeating geometrical
pattern.

In the course of excavations carried out in
1961-63 and then again in 1982, the remains
of a late Roman villa as well as some mosaic
fragments were discovered near Nagyharsány
in the south of Hungary. The findspot is at
a distance of thirty kilometres south of
Pécs, a flourishing town of the Roman
province Pannonia, called Sopianae at the
time that has proved to be rich in
outstanding archaeological finds since then.
The results of archaeological
investigations proved that there had been a
kind of continuity of urban life and
religious communities up to the period of

the establishment of the Christian church
of the Árpád dynasty.

During the excavation several Roman mosaic
panels of figural and geometrical design
were lifted, among others a geometrical
mosaic of black, white, red and ochre
tesserae, the size of which is 25ox9o cm.
Owing to previous disturbings and earthworks
only the above-mentioned mosaic has
survived. Therefore we could not count on
the existence of any further mosaic
fragments which could have been joined to
this piece. Our aim was to stabilize the
existing fragment retaining its authentic
and aesthetical qualities by a relatively
quick technology, looking for lightweight
but solid materials so that the mosaic could
be handled easily and presented vertically.

Figure 1 Separating the temporarily
stabilized mosaic surface from the terrazzo
embedment

Facing-up was carried out by sticking three
successive layers of gauze on the cleaned
mosaic surface with "Budaplast" /an
aqueous dispersion of polyvinyl-acetate/.
A flexible, thin wood-fibre panel was pushed
gradually in between the temporarily
stabilized mosaic layer and the terrazzo
underneath it. The mosaic separated from
the ground in this manner was carried to
the Restoration Laboratory of the Hungarian
National Museum.

In order to fulfil our aims we first tested
the method on the surface of a separate
mosaic fragment of 3ox6o cm from the same
findspot. The experiences gained herewith
were utilized in the restoration of the
bigger mosaic.

In the laboratory the mosaic was gently
slipped onto panels covered by polyethylene
sheets with its face downwards. The
protuberant terrazzo remains on the back
were removed by a vibration chisel and
clawed steel tools. The missing tesserae
were temporarily replaced by "Poromix" and
"Hungarocell" cubes of appropriate size
following which the synthetic replacements
were covered by blotting paper impregnated
by Budaplast, so that the spots of the
missing tesserae should be isolated from
the epoxy-resin layer which was meant to
fix the support later on.

A frame of 21ox7o cm was then constructed
from 3 mm thick Tee-sections /6ox3o mm
each/ made of hard aluminium, reinforcing
it by struts in the longitudinal and lateral
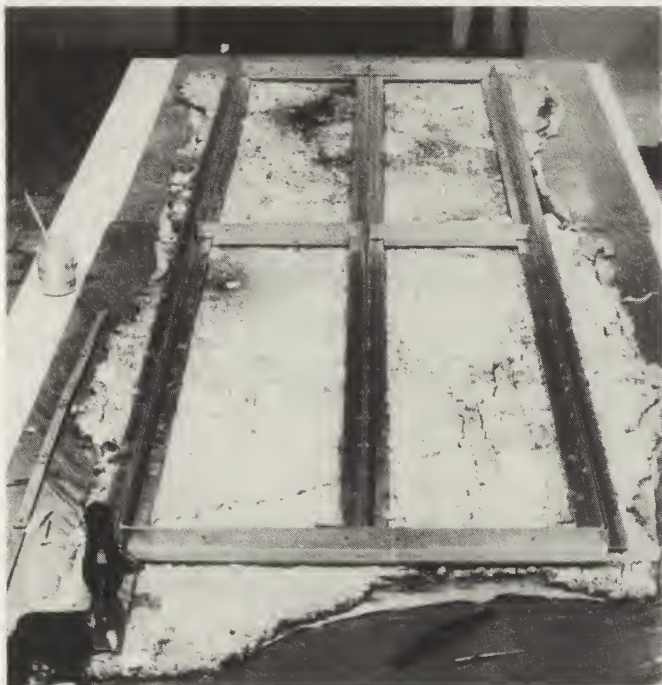axis. In the cross direction holes were

Figure 2   The assembling of the aluminium support for the backing of the mosaic

Figure 3   The placing of Hungarocell cubucles to fill the missing tesserae

drilled every 8th cm in the long holders into which hard aluminium wires /diameter: 4 mm/ were placed in parallel.

The framework prepared in the manner described above was then put aside and the uneven surface of the back of the mosaic

Figure 4   The process of consolidation of the back. A: the already cleaned reverse side; B: first layer of epoxy resin and glass wool; C: second layer of epoxy resin and glass wool.

Was made even by filling the lacunae with epoxy-resin made thixotropic by aerosil and flaked asbestos. After this two layers of flaked glass-wool with epoxy resin were laid on the back by pressing them into it through a thin polyethilene sheet. Both the double layer of glass-wool and the back of the mosaic became sufficiently impregnated by the epoxy resin and the pressing of the surface repeated several times during curing brought about a solid, homogeneous system.

Now came the phase of fastening the framework to the mosaic itself. Thixotropic Eporezit was laid on the surfaces of the framework to be attached to the mosaic /for this purpose Hungarian made Eporezit R-3 was used as an adhesive and Eporezit FM-2o for casting/. The aluminium reinforcement was joined to the back of the mosaic by the adhesive resin under load. Since the vulcanizing of the Eporezit-glass-wool system on the back of the mosaic had not yet finished, the joint curing of the adhesive resins applied at different times was ensured. Further reinforcement of the frame was established by the laying of additional flaked glass-wool strata impregnated by synthetic resin. These aimed at joining the back of the mosaic with the horizontal parts of the Tee-sections as well as with the hard aluminium wires at a distance of 8 cm each. In this say we succeeded in forming a solid system of mosaic-glass-wool-aluminium frame stuck by epoxy resin, providing sufficient reinforcement for the reconstruction of the mosaic. The final hardening of the whole system was brought about by the joint curing of the above layers under load for 16 hours.

The mosaic thus stabilized was then turned over and the temporary stabilization, i.e. the gauze stuck by Budaplast used for facing-up was removed and the surface cleaned. The synthetic foam used for filling the lacunae was also cleared away. The repetitive geometrical pattern allowed us to complete the losses without risking misinterpretation by tesserae of matching colour gahered from the excavation debris. For sticking the above mentioned thixotropic epoxy-resin was used.

In the field of the mosaic squares of 23x23 tesserae are to be found, with alternating cubes and Solomon's knots in a black background, with plain white fields of 11x23 tesserae in between them. The average size of the tesserae is 12x12x12 mm. Since the above pattern can be seen repeatedly on the mosaic, there was nothing to justify further reconstruction along the edges. We did not intend to give it an oblong shape or attach it to such a frame, either. The support applied made it possible to show just as much as we had found, no more, no less.

The length of the assembled mosaic is 25o cm, its greatest width is 85 cm. When assembling it we measured the weight of the different materials and chemicals. The weight of the aluminium frame is 8,8 kg, that of the glass-wool and flaked asbestos 1,4 kg, while the synthetic resin Eporezit weighed 11 kg. Since the weight of the reconstructed mosaic block is 54 kg, the net weight of the mosaic is 32,8 kg.

As it was stressed beforehand, for the stabilization process only the minimum amount of consolidant and adhesive materials were used in a new composite, all of which have proved to be successful both in industrial and restoration practice. There is no separation layer in between the
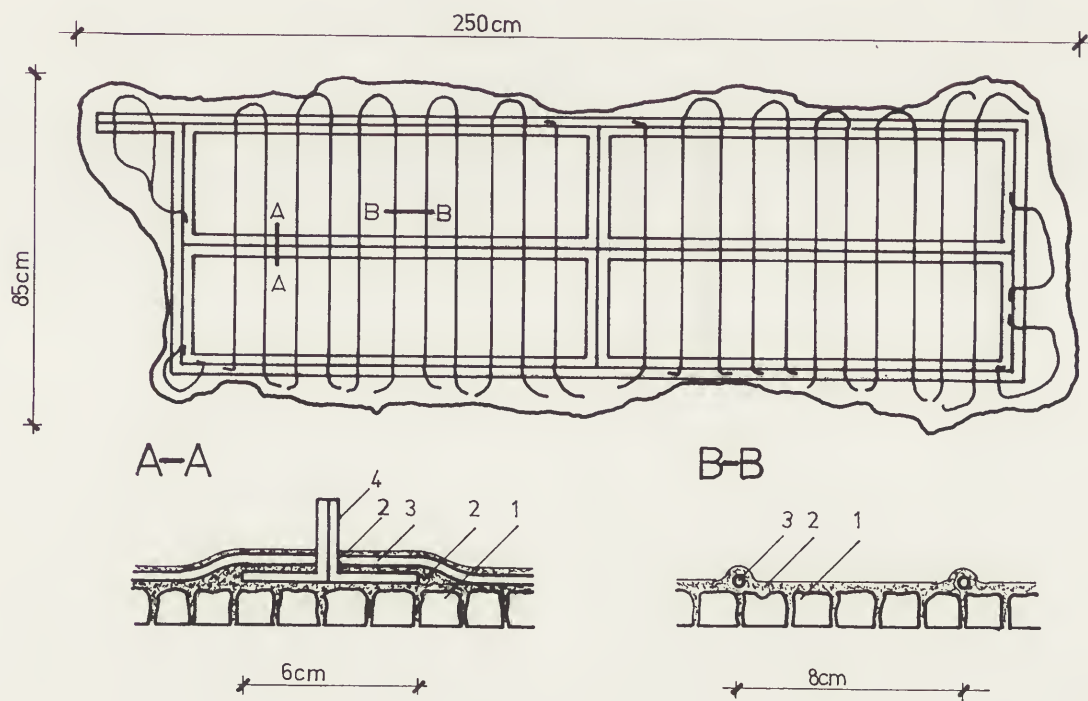
Drawing 1   The structure of the aluminium support for the mosaic: enlarged A-A B-B section.
1: mosaic; 2: epoxy resin containing glass wool; 3: aluminium wires; 4: reinforcing aluminium
frame of Tee-sections

Figure 5   The back of the consolidated mosaic

mosaic and the reinforcement since in the
given instance this would have increased
the weight of the system as well as
statically weakening the reconstruction.
In the same manner, under the circumstances
described above in consultation with the
archaeologist - with the aim of recon-

Figure 6   The cleaned face of the mosaic after
completing the lacunae

Figure 7   The face of the mosaic after
removing the temporary gauze layer

struction in mind - we did not deem it
necessary to enforce the possibility of easy
reversibility - i.e. the disassembling of the
mosaic - as proposed to a method providing
means for the authentic and aesthetical
presentation of the find in question.

TWENTY YEARS OF BARIUM APPLICATION ON MURAL PAINTING. METHODOLOGY OF APPLICATION.

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SUMMARY

The purpose of this report is to illustrate
how and when method should be used for the con
solidation in mural paintings. The basic metho
dology is described (materials, times and me-
thods of application). Two combined operations
(cleaning, based on Ammonium Carbonate, and
consolidation based Barium Hydroxide), can in-
tereact to create new chemical components whi-
ch result appropiate for the conservation of
mural paintings. Variations in the application
of this method are illustrated, according to
the support, painting technics and degradation
The most appropiate weather conditions for ef-
ficient results are indicated. In summary a
critical analysis on the behaviour of this o-
peration over a period of several years is ma-
de with respect to other technics of consoli-
dation. All the phases of the operation as wel
l as various examples carried out on specific
paintings in the last years, are shown through
a serie of photographic documentation.

As it is know the consolidation of a mural pa-
inting is necessary when the pictorical layer
has separated from its plaster support. The
reasons can be varied nature. The operation
consists of recreating the adhesion between
the two separated layers, riconstructing a ho-
mogeneous surface and restoring to the motar
the caracteristics it has lost. The most cospi
cuous and diffused motive for degradation is
the process of solfitization of lime carbonate
Past techniques were inclined twards the tea-
ring away of the painting or fixing with adhe-
asive substances of organic or synthetic natu-
re. These remedies more than often have inef-
fective results. The stimulus for a technolo-
gical research directed at finding a sound me-
thod against the effect of the lime solfate in
mortar. It was in the period of the florentine
flood in 1966 when restorers and scientists
colaborated uniting their knowledge. This mi-
xed research group demonstrated the possibili-
ty of stopping the process of solfitization
reconsidering barium hydroxide which had in
the past been used for the consolidation of
stone but had never been considerd for appli-
cation to mural painting. To effectuate the
consolidation one must take advantage of the
carbonization of barium hydroxide which forms
a mineral cement, Barium Carbonate.(see the
relation of the Professors E.Ferroni, V.Mala-
guzzi-Valerj, G.Rovida).However they used ba-
rium hydrate to transform lime solfate into
barium solfate, a substance which is innert
and insoluble. This was obtained with an inter
mediate reaction using Ammonium Carbonate.
From a theoretic point of view the effect of
barium hydroxide combined with reagent ammoni-
um carbonate for some time already used in cle
aning. The problem at that moment was to find
a method of application of the barium, avoi-
ding the effect of patina on the pictorical
surface, esthetically inceptable and caused

by the formation of barium carbonate on the
painted surface. Through experience it was de-
cided that cellulose-pulp was the ideal means
for this operation. Previously we had tried
using packs with other supports for the barium
hydroxide some of these being, cotton wool,
polverized fossil, filter paper, altapulgite
and bentonite etc. Each case presented the
problem of an excessive velocity in the tran-
sformation of the solution from the pack to
the plaster; an irregularity of the treated
surface plus a conseguent carbonatization of
the surface and the relative fenomenon of whi-
tening. Whereas the cellulose-pulp added to a
saturate solution of barium hydroxide and wa-
ter, was able to guaranted the penetration of
water avoiding the immediate reaction of the
barium hydroxide with atmosferic carbon dioxi-
de, on the pictorical surface; in this way the
eventual external carbonization happens only
on the surface of the pack. Eliminating the
inconvenient superficial crystalline veil.
The cellulose pulp has noteable malleability
permitting uniformity of application and adap-
tability to irregularities in the pictorical
surface. The thickness of the application can
be regulated in accordance with the ammount
of solution to be applied. Once it has dried
the pulp is light and easily removable and is
not prone to contractions and formation of
craquelle fenomenons which are common in other
pack-supports. Obviously the barium hydroxide
pack treatment is executed after the fresco
has been cleaned. This operation varies from
one case to another according to the type and
state of degradation. The treatment with Bari-
um hydroxide is carried on in three phases:
- The application of a sheet of japanese rice
paper on the pictorical surface (using only
water as the adhesive), this is to avoid any
direct mecchanical action of the wood cellulo-
se-pulp on the pictorical film. Infact the pa-
per blocks the detached surface layer protec-
ting it. Allowing the successive operation
with the cellulose-pulp to be carried on under
safe conditions, that is no risk of loss to
the painted surface. The rice paper also per-
mits us to remove the pulp when removing the
underlying paper, which has acted as an iso-
lant.
- Application of the cellulose pulp which is
soaked with a saturate solution of barium hy-
droxide. This operation is carried out star-
ting at the base and working upwards: appli-
cation must be homogeneous and compact to avo-
id leaving parts uncovered, forming a white
veil. The water content of the pack must not
be excessive to the amount the pulp can absorb
avoiding the solution dripping on inferior zo-
nes of the painting.
- Removal of the pack.
The correct period of contact of the pack is
considered that in which the major part of the
saturate solution of the barium hydroxide pe-
netrates into the wall, but not to the point
in which the pulp is completly dry. A retard
in the removal can provoke excessive rigidness
of the pulp and a strong adhesion between the
pictorical film and the pulp, provoking the
danger of tearing away small areas of the pic-
torical film. To remove the pack too soon pro-
vokes the formation of a layer of condensation
between the surface and the pack and therefore
an opalized veil ($BaCO_3$) on the surface, which
is irreversable. It is important to keep in
consideration the seasonal period best suited
to carry out the consolidation. The best sea-
son is autumn when the walls are reabsorbing
the humidity lost during the hot summer months
However it can be effectuated from autumn to
spring when the hypometric conditions of the
wall allow the saturate solution to be absor-
bed well into the mural support. In excessivly
warm weather, we have the fenomenon of a super
ficial cristallization,which gives much less
satisfactory results.

Application of barium in the various cases

A typical case in which we should apply barium is when the painting demonstrates the presence of solfates and the consequent lifting of the pictorical layer. Even When these fenomenons are not present, this operation of consolidation is always preferable after cleaning with a reagent. Often infact there is a noted hardness of the material after the evaporationof the cleaning agent and the drying of the surface. The barium in this case unites with the original medium riconsolidating the material. Besides the fact that the operation of restoration is conditioned by the necessity of a consolidation of the pictorical film the first operation to be carried out is the cleaning. This can be done by diffusion with the cellulose pack soaked with ammonium carbonate or by direct contact with ammonium carbonate in a supersaturate solution, or with other supports, which have the characteristics to diffuse the saturate solution uniformly on the surface. With this operation we fulfill two aims: the cleaning of the painting and the transformation of the lime solfate into soluble ammonium solfate. It is important during the operation to apply between the pictorical film and the support a sheet of rice paper, to avoid any mechanical damage of the painting The cleaning must be carried out with particular attention on colours containing copper such as the greens and blues which can be altered by the reagent. When the cleaning has been carried out the surface must be rewashed with distilled water.When it is dry we can proceed with the consolidation using barium hydroxide.

Fresco painting in the fifteenth century

Often we find painting in the fresco technique but with colours mixed with lime white (white wash). Some artists added to these pastes of colour organic substances for example milk which allowed a freer and more fluid brush-stroke. In these cases the barium can be an obstacle to an effective penetration on the inside of the porous structure. The hydroxide slowed down in it's penetration can react with air and form an opalized veil on the surface. An attentive analisis of the material can avoid this inconvenience. The methodology relative to cleaning in these cases assumes primary importance. We proceed with packs of cellulose-pulp and ammonium carbonate rather than simple superficial applications. In this way we are able to create with uniformity, a series of capillary pores which promote a better penetration of the barium into the support, avoiding the superficial opalized veil.

Tempera painting

We intend here for tempera painting, painting carried out on a smooth dry wall, with colour united with an organic medium. In the presence of solfitization we can proceed with the same method used on frescos after we have tested the stability of the colours in relation to the alkaline action of lime. During treatment of the barium pack these can undergo transformation and discoloration. Experience bring us to the conclusion, however, that the operation with $Ba(OH)_2$ should be anticipated with a pack of ammonium carbonate, but only after a wide range of tests on small zones of the painting to verify the precise reactivity to the reagent. The action of the ammonium carbonate takes place on the cristalls of the lime solfate which are dissolved in ammonium salt and on the organic adhesive of the colour which is temporarily softened. The surface of the colour demonstrates due to the presence of solfitization an unsticking and alteration of the organic medium ‚which makes the pictorical surface more porous. The ammonium carbonate is able to penetrate into the wall carrying out it's first actions on the plaster , this also provokes an ulterior growth in the porousness

which consents in this way a uniform penetration of the barium hydroxide. By capillarity during the successive pack, the $Ba(OH)_2$ ricomposes these pores by carbonization and recreates the compact structure of the surface, as well as transforming the ammonium solfate into inert barium solfate (it's principal characteristic). All these operations apart from the one concerning the solfate cristalls, are not macroscopic and therefore visible, so the painting has not beenrvisibly altered. What has been definitivly maintained is the elimination of the process of solfitization of a substance compact and homogeneous.

Paintings with whitewash from 16th to the 18th century

This does not present any particular difficulties as far as the inorganic medium is concerned, it is a materia homogeneous to its support. It is a material more porous than a "buon fresco" and therefore variations in temperature contribute more to degradation by solfitization and peding of colour. As result we find painting completly detached even in profundity In accordance with this we will give an example of a painting, a case which we consider a good indication to demonstrate the efficiency of barium even in the presence of a solfitization so extreme that the recuperation of a legible immage seemed impossible. We speak of a painting of the sixteenth century in the cleister of the Museum of S.Marco in Florence. The extremely fragile consistance of the pictorical film of the whole surface did not consent the use of a pack,but made necessary certain precautions to avoid the loss of pictorical material by mecchanical action, essential for applying the cellulose-pulp to the painting. We prefered to delicatly apply a sheet of rice paper to the wall fixing it with a saturate solution of ammonium carbonate applied by tampooning with cotton or a spunge. With this operation the water penetrated the wall and drew the fragments of colour back into adhesion with the wall. The saturate solution of ammonium, penetrating the wall transforms the solfate of lime into solfate ammonium which is more soluble and therefore allows the tampooning action to reorganise in their original places, the scales of colour that were lifted by the pressure of the lime solfate. Contemporaneously the layer of superficial dirt which would have been impossible to remove because of the delicacy of the pictorical surface is lifted like in a normal operation of cleansing, and after beeing solubilized by the solution can be absorbed by the tampon, through the rice paper. After this cleaning the surface is rewashed with distilled water using the rice paper as a filter; the surface is dried and we pass to the second part which would be consolidation which consents the solitary pack of cellulose-pulp and barium hydroxide. The adhesion of the pictorical film to the mortar and the cohesion of the mortar, is in this assured, stability. The notable discohesion that the painting presented required various acts of consolidation. The experience with barium over almost twenty years, permitts us to consider it valid for all the paintings treated as much as their stability in relation to the process of solfitization even, when exposed to the air in external areas is subjected to the direct action of atmosferic pollution. The cromatical quality apnears as brillant and compact as it presented itself immediatly after the operation. The validity of barium has been seen also during the phases of tearing and separation of frescoes ‚in as much as the new cohesion of asportation in greater quantities. The use of possibility for new method ‚using new materials including barium itself. The new cohesion of the mortar and the new cristalline fabric constructed by the carbonated barium determining minor porosity (however not eliminating it completely) allowing

a certain level of protection from pollutive
agents. The consolidation with barium is natu-
rally an irreversible process. This reopens
the debate concerning the reversibility of the
processes of restoration also in the case of
consolidation and it becames a purley theoreti
cal discussion. In fact there does not exist
any means eliminating a consolidation which
has penetrated into the porosity of the materi
al. The problem is based therefore on the ba-
sis of the choice of the most appropiate mate-
rials. Organic resinous materials can appear
more reversible, however the processes of alte
ration are more probable, for these than for
inorganic mineral materials. Above all we must
give consideration to the respect to natural
properties, of the work of art. Especially
where a consolidating agent is used as a pene-
trating factor in the material itself, without
any pratical means of removing it. In this ca-
se it is much better an operation which is sta
ble, durable and similar to the supportive ma-
terial. This is the reasons why the scientific
research for problems of this type should be
directed, more correctly, twards mineral, inal
terable substances. In appendix as an example
there is a detailed description concerning the
application of the method of cleaning and con-
solidation, one operation after the other with
all the indications relative to the methods.
The methodology is referred to a particular
example but substantially it is not different
from the method used for other mural paintings
The possible variations are relative, as it
has been explained to the absorbing capacity
of the mural support or to a particularity in
the technique of execution.
Experimental: An example of the process of
Barium is accuratley reported to illustrate
better evry step
Application of the "barium method" on a mu-
ral painting of the XVIII. century in the
refectory of SS. Annunziata in Florence.
I) Preliminary application of ammonium car-
bonate. For this particular kind of paint-
ing characterized by a very rough plaster
and by the presence of small and resistant
clots of solid particulate included in a
fatty patina (caused by the organic vapour
of the food), a preliminary application has
become necessaru and is effected in the fol-
lowing way: we prepared a supersaturated
solution with abundant base covering of am-
monium carbonate in distilled water. As a
matter of fact the crystals of ammonium car-
bonate facilitate the contact of the poul-
tice used for cleaning. At last we applied
by brush the above mixture directly on the
pictorial surface.
2)Poultice with ammonium carbonate.
Proportions of the poultice:(Unit of weight)
IOO parts of cellulose-pulp saturated with
water.
50 parts of solid ammonium carbonate in
crystals. The two components have been amal-
gamated by taking care of effecting a quite
uniform dispersion.
The application has taken place by hand,
from the botton to the top, by guaranteeing
a thickness of 0,4/0,5 cm. The contact time
of the poultice was of 5 h. With exception
of some parts where the colour appeared to
be weaker, the poultice was spread directly
on the surface without interposing the usual
sheet of Japanese paper. So we avoided the
danger of detachment of the cellulose-pulp
from the very rough surface.
At the end of the five hours lasting con-
act time we proceeded to the removal of
the poultice by starting from the botton to
the top in small portions and by meaving an
edg of about 2 cm. at the margins. This ser-
ves to limit the diffusion of the solvent
for the next poultice that of course will
have this edge as border. The removal of
the substances not belonging to the painting

Is effected with the help of cotton and a
small natural sponge, everything soaked
with water saturated with ammonium carbona-
te. Once the operation was ended, we pro-
ceeded to the cleaning of the whole pain-
ting by means of distilled water. The trea-
ted surface measures 70X50 cm., and on it
were used 2,4 Kg. of material composed as
follows:
-Cellulose-pulp saturated with water: I,6
Kg.
-Solid ammonium carbonate in crystals: 0,8
Kg.
After the application the poultice showed
a loss in weight of I,75 Kg. (about 73%).
The water content of the saturated pulp
was evaluated by weighing it before and
after a drying out in a stove at 60° C.
So a water content equal to 88% was ascer-
tained. (referred to IOO parts of pulp sa-
turated with water. The use of acid ammo-
nium carbonate on a painting with pigments
based on copper may be considered as more
suitable because the water solution of this
compound supplies by hydrolysis a lower
concentration of NH_3 by making in such way
less probable the formation of the soluble
cuprammonium complexes.
For this purpose it is also necessary to
reduce the contact times.
3) Poultice of barium carbonate:
After a period of about I5-20 days from the
end of thecleaning operation, we started
the reinforcement by means of barium hydro-
xide. This last operation is to be effected
only after the ammonium carbonate has fully
evaporated in order that the result be sati-
sfactory. Methodology followed:
A) With distilled water we applied by brush
a japanese rice paper in the pictorial sur-
face.
B)Along theoutline of the surface expected
to be treated we applied an edge of about
2 cm. of cellulose-pulp soaked with distil-
led water in order to aoid any possible mar-
ginal carbonatations beyond the surface co-
vered by the pulp.
Proportions of the poultice:(Unit of weight)
-IOO parts of cellulose-pulp saturated with
water.
-I5 parts of octohydrated barium hydroxide.
We amalgemated the barium hydroxide with
the cellulose-pulp by mixing Very carefully.
During this operation it is indispensable
to use gloves owing to the toxicity of ba-
rium. The spreading of the material proce-
eds from the bottom to the top according to
a thickness of about 3 mm. The contact time
varies from four to five hours, the treated
surface measured 55X45 cm. On it were used
0,7475 Kg. of material composed as follows:
-Cellulose-pulp saturated with water: 0,65
Kg.
-Octohydrated barium hydroxide: 0,0975 Kg.
After the application, the poultice showed
a loss in weight of 0,5075 Kg. (about 68%).
The removal of this poultice has been ef-
fected from the bottom to the top in small
portions. The cellulose-pulp used showed the
same water content as the previous poultice.
It is important to note that with regard
to the normal times of application we must
prepare not more than I Kg. of poultice ma-
terial; larger doses would involve the car-
bonatation of barium hydroxide in the con-
tainer and therefore if we ahould use the
poultice after this reaction, an irrever-
sible whitish patina would be caused on
the pictorial surface.

Photos by Sergio Cipriani

Fresco and particular from the XVI° century cloister of San Marco, Florence.
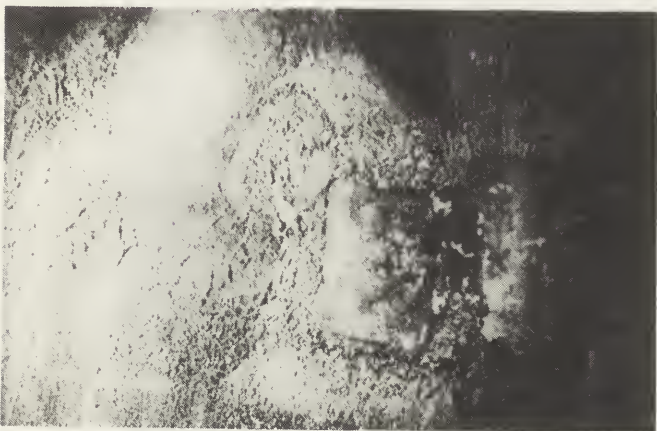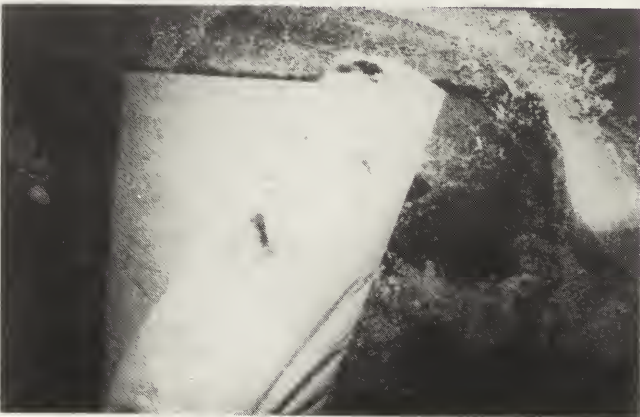

1) Part: Detached colour due to sulphatization.
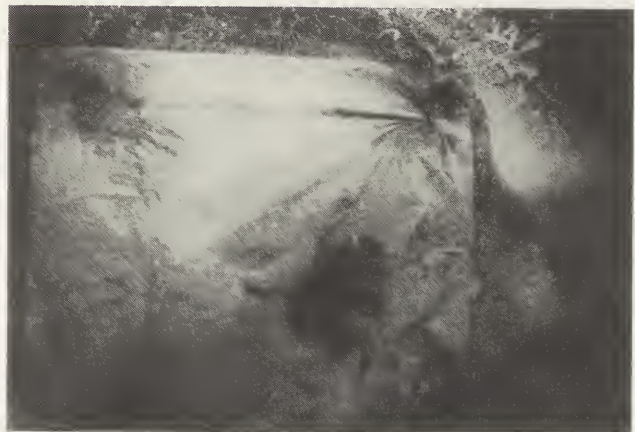
2) Application of Japanese rice paper to protect the painted surface.

3) Tampooning with sponge. Almost triple action: readhesion cleaning of the painting, chemical transformation.

4) Removal of Japanese rice paper.

5) (A) Already consolidated (B) Still detached

6) part of the fresco after the treatment with barium hydroxide.

Part. of a fresco from the XVIII century Refectory in the convent of S.S. Annunziata Florence.

7) Before the cleaning

8) during the cleaning

9) after the consolidation with barium hydroxide

Part of the fresco by Beato Angelico of the chapter in the cloister of S. Marco, Florence

IO) Part. of the fresco by Beato Angelico taken in grazing light

11) as (10) after the cleaning
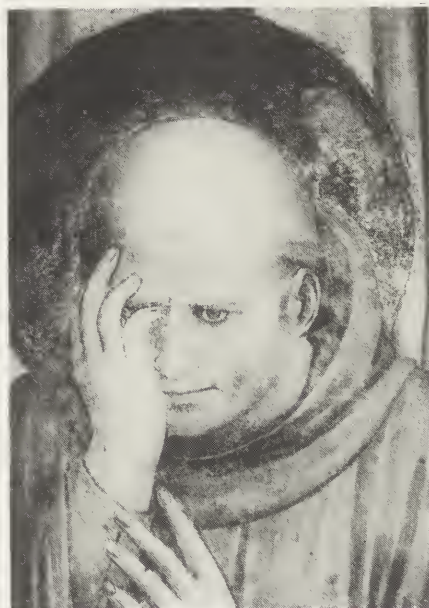

I2) As (IO) after the consolidation with barium

part. of fresco from the XV° century laboratory of restoration-conservation of mural paintings.

I3) part. taken picture in grazing light before cleaning

14) visible the cleaned part.

Part of a fresco from the XVIII° century Refectory in the convent of SS.Annunziata, Florence.

17) during the application of ammonium carbonate, applied with brush.
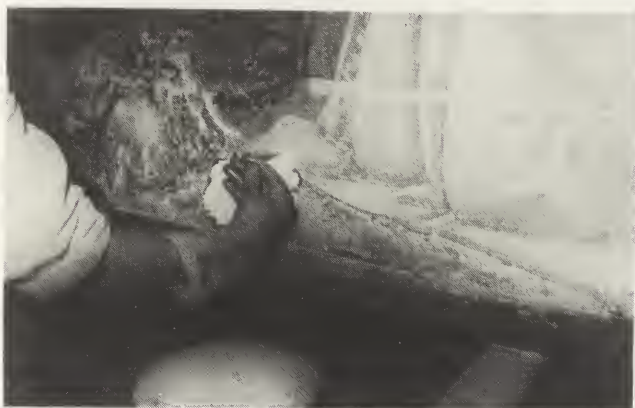
15) application of the pulp-pack with barium hydroxide.

18) application of cellulose-paste with ammonium carbonate.

19) after the cleaning.

I6) remotion of the barium - pack

20) preparation for the consolidation with barium hydroxide.

THE TREATMENT OF TWO THIRTEENTH CENTURY CHINESE WALL
PAINTINGS IN THE COLLECTION OF THE ROYAL ONTARIO
MUSEUM by Eric Gordon*and Elizabeth Phillimore**

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**Royal Ontario Museum
 Toronto, Ontario Canada

SUMMARY

Homage to the First Principal, two thirteenth
century Taoist Chinese wall paintings in the collec-
tion of The Royal Ontario Museum (ROM), recently
underwent extensive analysis and conservation. In
the early part of this century, the paintings were
cut into numerous small blocks and taken from China
to Japan. There, the support material was removed and
the paint layer mounted onto paper and muslim panels,
six to each painting. The panels were brought to
New York and acquired by the ROM in the 1930's. In
Toronto, the paintings were mounted onto masonite,
three sections for each of the six vertical panels,
thus totaling eighteen masonite. panels per painting.
The panels were then screwed onto mahogany grids and
mounted onto walls in the museum.

The 1980's conservation treatment attempted to re-
secure the numerous support layers without disturbing
the adhesives and materials used in previous treat-
ments, remove surface dirt, discolored resins, over-
fills, retouchings and overpaints and with the aid of
early documentation and art historical research,
inpaint the block joins and reintegrate the most dis-
figuring losses. The paintings could be treated
horizontally or vertically because of the earlier
divisions and mountings, thus facilitating all stages
of the treatment and allowing for innovative tech-
niques. Cleaning was carried out under individualized
plexiglass fume extraction chambers, and cleavage was
set down under wire-less fiberglass heat blankets
using an acrylic emulsion.

The Royal Ontario Museum (ROM) has in its collection
three rare thirteenth century Chinese wall paintings.
Recently, two of these, together titled Homage to the
First Principal, were extensively treated by a team
brought together for this specific purpose. Art
historical research and contact with the owners of
similar paintings, including those in China, was
simultaneously carried out by the ROM's Far Eastern
staff, while in Ottawa, the Canadian Conservation
Institute analyzed pigments, mediums and support
materials of the original and its restorations.

ICONOGRAPHY, EARLY HISTORY, CONSTRUCTION
The two paintings are individually titled Lord of the
Southern Dipper (west wall, 10'5" x 34'1") and Lord of
the Northern Dipper (east wall, 10'4" x 33'6½"). They
depict celestial beings moving at a leisurely pace
amongst clouds in an ethereal world. The composition
on the east wall moves from right to left, while the
west wall is the exact opposite. This arrangement
suggests a third composition representing the Highest
Power which would appear on the north wall and to
which both processionals pay tribute. A still
standing temple from this period with similar wall
paintings in south Shansi, at Yung-Lo attests to
this arrangement.

The west wall procession is grouped around three large
central figures: the Jade Emperor in the center; Lao-
tzu, the founder of Taoism, to his left; and the
Empress of Heaven to his right. Among these figures
are smaller attendents holding fans and banners. At
the lower right is the Lord of the Southern Dipper
(Sagittarios) with his fierce tantric attendant. They
are followed by nine officials representing the nine
stars of the Southern Dipper. These officials are
followed by two smaller attendents carrying an alter
which holds a bowl with a white peony. To the left
of the central group are twelve astrological figures
wearing animal symbols on their headdresses, and
representing the twelve terrestrial Branches, part of
the sixty year cycle of the Chinese temporal system.

The east wall procession is also grouped around three
large figures: the Yellow Emperor in the center; the
Heavenly Emperor to his right; and the Empress of
Earth (wearing in her headdress the I-Ching trigram
for earth) on his left. Again, smaller attendents
float among these figures holding banners and fans.
Leading the procession is the Lord of the Northern
Dipper (Ursa Major) with his three-faced, six-armed
tantric attendant, followed by seven figures in black,
representing the stars of the Northern Dipper. They
are followed by two attendents carrying an alter
bearing coral on a golden tray. The last group on
the right consists of the Planetary Dieties: Venus,
Jupiter, Mercury, Mars, and Saturn, each bearing their
associated symbols.

The murals were painted in the Yuan Dynasty (1279-
1368), a period of great religious freedom. Buddhist
and Taoist iconography and symbolism were liberally
intermixed in the sculpture and paintings decorating
the temples. It is not certain from which temple the
paintings were taken, however it is known that the
complex was in the south Shansi province, and in all
likelihood, the murals were designed by the master-
painter who worked at nearby Yung-Lo. The Master's
school prepared the walls, first applying loess clay
mixed with bamboo splinters onto a free-standing wall.
When this first layer was dry, clay mixed with chopped
hemp was applied, followed, when dry, by a final coat
of finely washed clay. On this top surface, the
master-painter outlined the overall, final design in
black, and with the assistance of his pupils, filled
in the lines with local color. On close observation,
minor changes in the original design were noticed on
the ROM's paintings, where color was applied over a
black line.

The paint medium has not been satisfactorily identified,
but it is thought to be a gum solution. The gum medium
was mixed with pigments whose particle size affected
the depth of color. The blues were azurite; browns
were hematite; yellows were goethite; reds were
vermillion, hematite and minium, alone or in combina-
tions; whites were kaolinite and quartz; and flesh
tones were combinations of vermillion, hematite,
minium, quartz and kaolinite; the black has not been
identified. The greens are now copper oxalates with
slight traces of malachite. However it is thought
that a chemical reaction occurred which almost com-
pletely converted the original malachite to copper
oxalate hydrates.[1]

The paintings at the ROM, like those at Yung-Lo, are
elegantly stylized and traditionally two-dimensional.
Little to no modeling of form occurs within the black
outlines except inside the six large opaque halos.
Here there are often gradations of intense colors,
suggesting the power of these beings. The other celes-
tial beings wear colored, transparent halos, tinting
what is behind them the color of the halo. Numerous
meticulous details, such as scaly dragons, hairy
monkeys, striped tigars and wave-patterned oceans
cover the paintings. However in total, one is im-
pressed by the rhythmic movement and grace in line and
color on a monumental scale.

DAMAGE AND EARLY TREATMENTS

Through the centuries the wall paintings were subjected to a series of natural and man-made disasters. Stains and water changed the tonality of the paintings, darkening and/or lightening colors, adding transparency or opacity and caused large cracks to open on the figures of the Empresses, as well as through numerous other details. However man has been responsible for the more severe damage to the paintings. From early on, the paintings were defaced with graffiti, primarily peoples' names and advertisements. This graffiti has become impervious to solvents. However the greatest damage by far occured in the early twentieth century when each painting was chopped into approximately one hundred blocks and exported to Japan. Fortunately, cuts were narrow and carefully made to avoid faces. In Japan the paintings were reassembled for a photograph, then treated. The treatment was written down in Japanese and given to the ROM when the paintings were acquired in 1937. The treatment was the following:

1. Clean each block, shellac and face the surface with rice paper; apply more shellac as an adhesive.
2. Soak each block in water to remove the clay support. Fill losses with a mixture of Tonoko (sanddust), Ishiwata (a mica) and glue (not specified).
3. Coat the reverse of each square with Funori (Japanese seaweed paste) then cover the paste with rice paper and flour paste.
4. Soak the square in alcohol to remove the shellac and facing tissue.
5. Mount with "hard paste" (not named) onto six large muslim panels which had been prepared with a rice paper and paste covering.
6. Spray with a "liquid" (not named) which had the capacity to "keep the layers tight together permanently."

This treatment caused extensive losses which were partially disguised with overpaints in watercolor and oil paint.

In this condition, the two paintings on twelve panels arrived in New York in 1934. Through Yamanaka and Company Gallery, the ROM acquired the paintings along with the early photographs and documentation in 1937.

Upon arrival in Toronto, the paintings were mounted onto masonite, three pieces of masonite to each of the six vertical panels. Each Japanese paper/muslim panel was cut into thirds, saturated with polyvinyl acetate and mounted onto masonite under the weight of a press. PVA has been found throughout the layers of the support and the paint, and ridges have been left from the pressure of the press. Woodworkers at the museum constructed a mahogany grid on which the panels could be mounted, and holes were drilled through the painting and support layers and counter-sunk brass screws employed to fasten each separate panel to the grid. The screw heads were then covered with PVA/clay putty and inpainted. Other losses were also retouched.

PRESENT TREATMENT
Because of extensive renovations at the Museum in 1980, it became necessary to dismantle and remove the painting mounted on the west wall. At that time the mural was examined and found to contain numerous large areas of cleavage. Also, it was felt that the 1930's retouchings were overdone, discolored, "art-deco-ish" and slightly Westernized in order to sell in North America. Thus it was decided that since the painting had to be removed from the wall and it was in need of structural and cosmetic work, the west wall mural and perhaps the east wall mural should have a complete, modern conservation treatment.

Before work on the paintings began, certain conditions had been established which influenced the course of the treatment. As previously noted, the paintings had to be removed from the wall. Also, they had to be transported to a laboratory outside of the museum to be worked on off-site. Lastly, a pre-determined

amount of money and time were established for the treatment. The present treatment proceeded as follows:

1. Face the paintings with wheat starch paste and Japanese tissue.
2. Remove screws from each panel and lift panel onto a padded wooden brace. This brace was employed in order to keep the panel from flexing during preliminary transport.
3. Remove panel from brace and screw onto plywood backing. This becomes one side of a plywood crate. The other sides are screwed into place and the crates are transported to the laboratory for paintings' treatment.

In the laboratory the treatment for each panel proceeded as follows:

1. Unscrew top of crate, leaving panel attached to plywood backing for extra strength and rigidity for duration of treatment.
2. Remove facing tissue with distilled water. Dissolve starch from surface of panels with .1% alpha-amylase enzyme (no. A-0273, crude, type X-A, from Aspergillus oryzae) in distilled water and remove excess with cotton and/or wooden tools.
3. Photograph panels in black and white and in color: overall; raking; ultra-violet; and details. An 8" x 10" xerox of the overall photograph was used as a pictorial examination report and treatment record. Cleavage, overpaints, cracks, screwholes, abrasion and areas which were being treated were all recorded in various colors on this reproduction.
4. Soften overfills with ethyl alcohol and water (1:1). Mechanically level or remove overfills with scalpel.
5. Remove overpaints where possible with ethyl alcohol: water mixture (1:1). An excess of water tended to dissolve the remaining clay support layer. The alcohol hastened the water's rate of evaporation and additionally dissolved some of the old retouchings.
6. Clean paintings and remove remaining overpaints with dimethylformimide and isopropyl alcohol mixture (1:1) under individualized fume hoods. Small plexiglass fume hoods with padded bottoms and one open end and one end conected to a large exhaust system were placed on a horizontal panel and cleaning was carried out using large swabs on long sticks while wearing protective gloves. The alcohol helped remove overpaints and also increased the evaporation rate of the DMF.
7. Set down cleavage with Rhoplex AC 234 (Rhom and Haas) in water (1:1), tacking iron, mylar and weights (cloth bags filled with #9 lead shot). For larger areas of cleavage, instead of heating with tacking iron, place Thermofilm[2] electric panel (a fiberglass electric thermal blanket with no elements running through center), felt and weights over area filled with Rhoplex, set blanket at low heat through rheostat and allow to dry. Rhoplex was chosen as an appropriate consolidant because it was most compatible with the previously used adhesives. It did not interfere with the PVA which saturated all the layers. Also Rhoplex flowed easily through all interconecting lacunae.

Small lead shot was used in the weights as it allowed pressure to flow equally over the contours of the panel.

The thermofilm is a carbon and fiberglass heat blanket enclosed in heavy mylar. No wire elements run through thermofilm and the amount of heat produced can be adjusted by plugging it into a rheostat.

8. Fill losses with clay, dry pigment and rabbit skin glue mixture, tinted to original clay color.
9. Rub two coats of 7% Acryloid B-72 in Super High Flash (a slow evaporating petroleum distillate) over panel over two day period. The varnish did not change sheen or surface quality of paintings.
10. Photograph panel in order to record what remains of the original and the extent of the damage.
11. Inpaint block joins and critical losses with Acryloid B-67 in varsol and dry pigments. Reinte-

gration based upon enlargements of early archival
photographs acquired along with paintings in '37.
Take after treatment photograph.

12. Screw three panels onto a section of the wood grid
    with brass screws. Cover screws and fill in cracks
    between panels with beeswax. Coat wax with Rho-
    plex AC   234 in water and aerosol and dry pig-
    ments (tinted to clay color), and inpaint with
    Acryloid B-67 in varsol and dry pigments.

13. Mount grid sections with panels onto wall in
    museum. Fill cracks between grid sections with
    balsa wood and beeswax, coat with Rhoplex mix-
    ture tinted clay color, and inpaint with Acryloid
    B-67 in varsol and dry pigments. Reintegrate most
    disfiguring losses.

CONCLUSION
The primary intentions of the treatment were to
strengthen the existing structure of the paintings
and to present an honest, coherent image. Upon
completion, it appeared that the adhesive used in
consolidation re-enforced the support system--
cleavage disappeared--and inpainting was restricted to
man-made losses and critical areas of design, which if
left untouched, would have immediately commanded the
viewer's attention--only cracks and paint losses
caused by nature remained clay color and were not in-
painted. Thus the paintings on the whole, do not look
"just painted," but rather appear as well-preserved,
thirteenth century murals.

The complete treatment of two Taoist paintings and a
superfacial cosmetic and structural treatment of a
thirteenth century Buddhist wall painting took five
full-time and thirteen part-time workers, interns and
volunteers two years to complete. The gallery
opened in November 1983.

NOTES

1. Analysis was carried out by Elizabeth Moffet and
    Neil Adair, scientists at the Canadian Conservation
    Institute, Ottawa, Ontario. Analysis was carried
    out by infrared spectrophotometry, x-ray diffrac-
    tion, x-ray fluorescence spectrometry, electron
    beam x-ray microanalysis (SEM/XES) and polarized
    light microscopy.

2. Thermofilm electric panel heating elements are
    made by Canada Thermofilm Ltd., 8421 Keele St.,
    P.O. Box 720, Concord, Ontario L4K 1C7, Canada.

TWENTY YEARS OF APPLICATION OF "BARIUM" ON MURAL PAINTINGS: FUNDAMENTALS AND DISCUSSION OF THE METHODOLOGY.

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SUMMARY

After about twenty years of systematic applications of Barium hydroxide on mural paintings in Tuscany, with the double aim of stopping "sulphatization" processes and reconsolidating disgregated plasters, the authors want to remark again this peculiar methodology which in every case gave only positive results.
The procedure is based essentially on three reactions, two of which are involved in a process that makes insoluble the sulphates present in the plaster. The third reaction meanwhile determines a consolidation of disgregated plasters through the formation of barium carbonate.
The whole process is critically revised and compared with other alternative procedures.
An extension of this method is proposed for the consolidation of other porous mineral artifacts.

INTRODUCTION

1966 is remembered by florentines as the "year of the flood". This was an extremely disastrous event not only for people but for the cultural and artistic patrimony of the town and of the world as well. Nevertheless, it constituted an important opportunity of incentive for the rationalization of many problems concerning the conservation of works of art which in that time were mostly only empirically considered.
Particular attention was dedicated to mural paintings which, due to their porous structure, had absorbed considerable amounts of water in the lower parts. This water, besides promoting dangerous solubilizations and recrystallizations of preexisting salts in the plaster, introduced new extraneous inorganic and organic materials into the porosity.
The revelant increasing of phenomena associated to the presence of salts in mural paintings stimulated a more active and specific research about the nature of saline products, their origin, and about the physical and chemical mechanisms through which they are acting.
The wide diffusion and strong gravity of a disgregating process which is originated by calcium bihydrate sulphate (Gypsum) was immediately evident.
Most of the destructive phenomena effecting the stability - i.e. cohesion and adhesion of paint layers - find their origin in the crystallization of limited soluble salts in proximity of the surface.
Plasters of mural paintings, due to their high porosity and hydrophile properties, are inevitably more or less imbibed with dilute salt solutions. If the dissolved salt is a not very soluble compound, there is a high probability that supersaturated solutions may be produced and that crystallization occurs.
Such a process may take place beneath the paint layers and the growth of crystals in small pores may determine a compression which progressively disrupts, lifts and detaches fragments of the paintings (fig.1).

The solution of a soluble salt is on the contrary much less subject to saturation and therefore the crystallization takes place only over the surface.
In this case the disgregating action is much less dangerous.
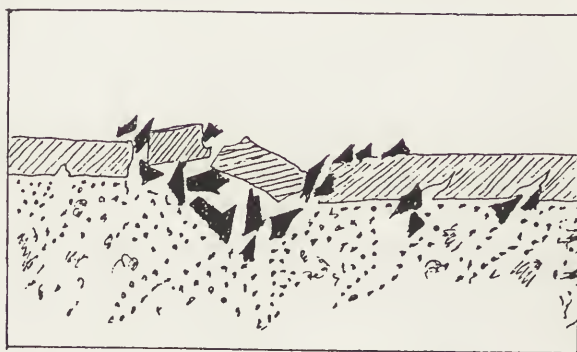Nitrates especially show this behaviour.

Fig.1 -
$CaSO_4.2H_2O$ ///////// paint layer   ∴∴∴plaster

salt		solubility at 20°C	
	g/100cc sltn.	molarity	relative to $CaSO_4$
$NaNO_3$	88.0	10.4	693
KNO_3	31.6	3.1	207
$Ca(NO_3)_2$	56.4	3.4	227
$Ba(NO_3)_2$	8.4	0.3	20
$NaCl$	36.0	6.2	413
$CaCl_2$	74.5	6.7	447
Na_2SO_4	44.0	3.1	206
$CaSO_4$	0.2	0.015	1

Tab.1 - Water solubility of some of the more common salts.

In table 1 the solubility of some more common salts that can be found in mural paintings is reported. One can observe that the solubility of Gypsum differentiates from that of the other salts as the lowest.
Relative solubilities of the other salts with regard to Gypsum (=1) show up values hundred times higher.
Gypsum is therefore one of the salts that with most probability may crystallize beneath the surface as well.
This phenomenon is known with the term "sulphatization".
Systematic analyses effectuated on a large number of mural paintings affected by the waters of the flood showed a wide diffusion of calcium sulphate. Analyses were usually carried out by X.R. diffractometry, a typical

instrumental technique for the characterization of solid samples.

A chemical procedure which could stop the disrupting action of Gypsum would have determined a decisive step forward in the conservation of mural paintings.

The problem was theoretically and experimentally studied by E.Ferroni and D.Dini (1,2,6, 10,13,14) who were able to find an appropriate methodology to neutralize the negative effects of Gypsum.

A chemical conversion of Gypsum into an inert salt was operated with the employment of ammonium carbonate and barium hydroxide.

Barium hydroxide - $Ba(OH)_2 \cdot 8H_2O$ - was already used in the past for the conservation of porous materials, particularly stone artifacts, but overall as a consolidating agent (3,4,5,7).

FUNDAMENTALS OF THE METHODOLOGY

Sulphates of alkaline-earth elements show a progressive decrease of water solubility with the increasing of molecular weight.

Barium salt is the less soluble $(1,03.10^{-5} M)$ sulphate in the series. Calcium sulphate is more than one thousand times soluble with regard to barium salt (fig.2).

The chemical conversion of the former in the latter corresponds to a drop of solubility of about 1440 times, in this way obtaining a compound that actually can be considered no longer soluble.
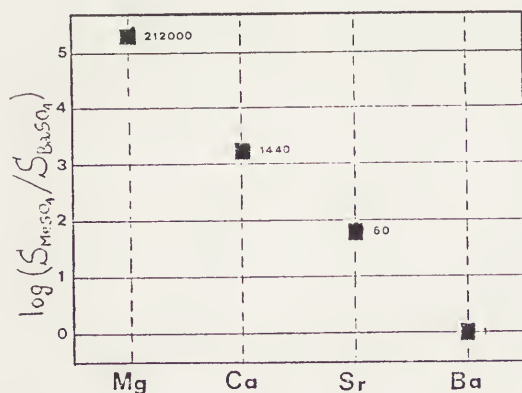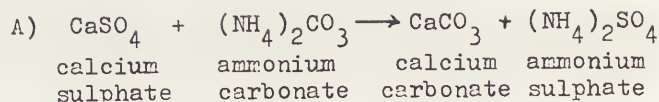
Fig.2 - Water solubility at 20°C of Mg,Ca,Sr and Ba sulphates; relative values versus $BaSO_4$ solubility $(1,03.10^{-5} M)$.

However the direct double-change reaction could not result completely effective:

$$CaSO_4 + Ba(OH)_2 \longrightarrow Ca(OH)_2 + BaSO_4$$

This reaction, due to scarce solubility of Gypsum and insolubility of $BaSO_4$, would involve only the surface of the crystals, the bulk remaining not transformed.

An intermediate step is then requested. Gypsum must be converted before in a soluble sulphate which, during a second step, may completely react with barium hydroxide. Ferroni and collegue found an appropriate intermediate stage determining the formation of very soluble ammonium sulphate.

Ammonium carbonate solution dispersed in a suitable pack was used as the reagent.

A) $CaSO_4$ + $(NH_4)_2CO_3 \longrightarrow CaCO_3$ + $(NH_4)_2SO_4$

calcium ammonium calcium ammonium
sulphate carbonate carbonate sulphate

The reaction, besides creating optimal physical conditions for the successive complete transformation to barium sulphate, determines a decisive regression of geometrical encumbrance volumes of Gypsum crystals as well.

Moreover the diffusion of $(NH_4)_2SO_4$ solution towards the porous contacting materials allows a very favourable dispersion of sulphate ions into the plaster and, better, into the pack.

A large amount of free sulphate ions are in this way eliminated.

The remaining part, now homogeneously distributed in the intonaco, is definitely converted into an inert compound through the following reaction (B):

B) $(NH_4)_2SO_4 + Ba(OH)_2 \longrightarrow BaSO_4 + 2NH_3 + 2H_2O$

    barium barium ammonia
    hydroxide sulphate
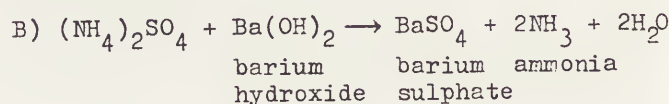
We must consider the two reactions A and B in more detail.

In the first reaction (A) calcium carbonate is produced as a secondary product. It is a normal component of plasters and therefore is absolutely consistent with the system. Excess ammonium carbonate which penetrates in the porosity of the mortar is not a problem. A slow autodecomposition of this salt spontaneously occurs:

$$(NH_4)_2CO_3 \longrightarrow NH_3 + CO_2 + H_2O$$

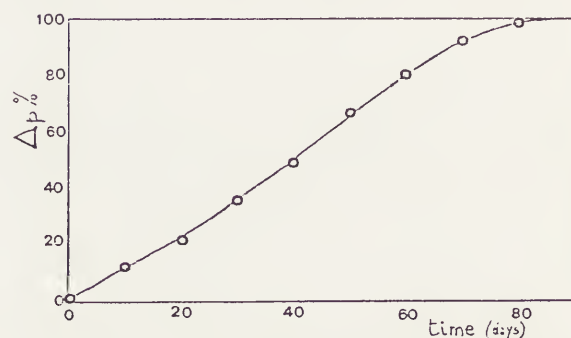The reaction products are all volatile and not dangerous compounds.

Fig.3 - Kinetics of decomposition of ammonium carbonate (20°C).

The kinetics of this decomposition was checked and the results are illustrated in fig.3 and tab.2. At room temperature a complete decomposition of ammonium carbonate in a few months occurs.

About the reaction B it was already pointed out the complete insolubilization of sulphate ion obtained through the conversion in barium sulphate.

The secondary products are again only volatile compounds which rapidly escape from the plaster.

t (days)	Δ w %
0	0
10	12
20	22
30	35
40	49
50	66
60	80
70	92
80	99

Tab.2 - percent loss of weight (decomposition) Δ w% of ammonium carbonate - open air - in a box, without ventilation, at 20°C.

Excess barium hydrate, homogeneously absorbed as water solution inside the intonaco, gradually reacts with atmospheric carbon dioxide producing an important third component (reaction C):

C) $Ba(OH)_2$ + CO_2 $\longrightarrow$ $BaCO_3$ + H_2O

    barium   carbon   barium
    hydroxide   dioxide   carbonate
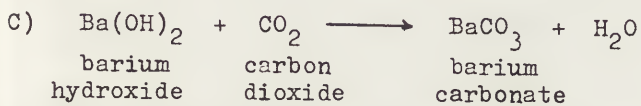
Barium carbonate, in this way produced, not only is not a problem for the conservation of plasters (it is in fact very similar to $CaCO_3$) but on the contrary it constitutes an excellent binding agent which may succeed in an effective consistent consolidation of the disgregate microstructures of intonacos.
The last (C) inevitable reaction proves to be after all, a securely advantageous step for the conservation of mural paintings.
This reaction is quite similar to that of calcium hydroxide in the setting of limes and mortars.
The critical point is the graduality of the process in order to obtain a well formed homogeneous texture of crystals, therefore avoiding any fast precipitation which otherwise would cause a whitening effect due to an excessive nucleation. Ammonium carbonate utilized in the first step (reaction A) of transformation of Gypsum is a well known effective cleaning agent for the conservation of frescoes. Its easy decomposability and therefore the possibility of a complete removal from plaster makes it a really appropriate cleaning product especially if compared with other soluble formulations containing not decomposable ingredients.
Porosity of frescoes constitutes indeed a not reversible trap for all that is soluble and cannot autodecompose.

Resuming what generically is known under the name of "methodology of barium" we can list and distinguish two fundamental steps:

A - PACK OF AMMONIUM CARBONATE

- accomplishes a preliminary transformation of Gypsum in a soluble sulphate - $(NH_4)_2SO_4$ - which partly is absorbed and partly homogeneously dispersed in the plaster
- operates the cleaning of the painting and allows the removal of overpaintings

B - PACK OF BARIUM HYDROXIDE

- converts the remaining soluble sulphate into inert and no longer soluble barium sulphate

- gradually consolidates incoherent microstructures of the paint layers and the plaster through a slow crystallization of barium carbonate.

DISCUSSION

The whole procedure of "Barium" is then quite different from a simple consolidating operation for mural paintings.
Most conveniently it may be considered a complete conservation methodology which, starting from the cleaning of the painting and the removal of overpaintings, operates an intrinsic general restoring of the structure including neutralization of sulphates and consolidation of plaster as well.
Understanding these general lines is of capital importance for any appropriate application of the method.
The "Barium process" requires a real experience and a familiarity with the several steps. A misinterpretation would be for example to consider it in the same way as a treatment carried out with resinous consolidants applied by brush.
On the other hand if the appropriate conditions are respected, positive results will be unfailing.
At present, after about twenty years of only positive results in the Tuscan area and elsewhere, the procedure is well outlined and may be rightly taken into account by conservators as a methodology of generalizable accomplishment.

Some care is required. The first step by ammonium carbonate is better carried out if a concentrated solution is used and a prolonged contact of the pack with the painting is allowed. These conditions will determine a high solubilization of Gypsum. In some cases the presence of delicate tempera-paintings may induce one to operate with shorter times and lower concentrations. A particular care must be observed for copper pigments as Azurite or Malachite. Excessive contact times may result in a partial solubilization of some pigment crystals in the form of cupric ammonia complexes.
Every time, therefore, it will be necessary to study the problem and consequently to adjust the procedure to the particular context.
The second step, by barium hydroxide, even if delicate, may be well accomplished if every opportunity of an accelerated carbonatization is accurately avoided.
While applying the pack the surface of the painting must be maintained quite protected from any atmospheric (CO_2) contact. This may be effectuated using crystalline octahydrate barium hydroxide homogeneously dispersed in a wood or cellulose pulp that was previously saturated with distilled water. The paste must have an appropriate consistence to allow its application and permanence on a vertical wall. Always a Japanese paper sheet is interposed. The paste will result sufficiently dense to prevent any permeation of carbon dioxide. The "barium" pack as well must have a prolonged contact time. This will allow a gradual homogeneous and deep impregnation of all porous layers. The consolidating action must gradually decrease from the surface to the bulk.

These and other conditions are essential for good results. If the whole operation is cor-

rectly effectuated sulphatization would be effectively stopped; incoherent, weak and partially pulverulent plasters will be converted in stable structures which now allow to be touched or to be wet without any danger.

In the past years the authors could regularly and closely follow a considerable number of restorations of mural paintings in which "Barium" was used.

A lot of analyses were always effectuated before, during and after the operations.

Many times, contingent situations such as a high porosity, the presence of delicate tempera finishings, a precarious cohesion, nitrate efflorescences, induced us to look for different times, concentrations, modalities, to obtain in any case good results.

"Barium" is not a reversible operation however no consolidating process is.

The application of a protective layer, an adhesive, a filling can result reversible but a consolidating agent cannot because it penetrates in the pores without any practical possibility of removal.

For such agents a physical, chemical and optical compatibility with the support is determinant.
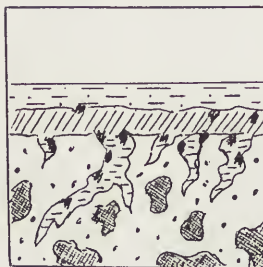

paint layer impregnated and disrupted by Gypsum (calcium sulphate ✦ ❙ ✿)
- paint layer ///////
- calcium carbonate ∴∵
- sand ▨▨▨

the paint layer is raised, the structure is incoherent.
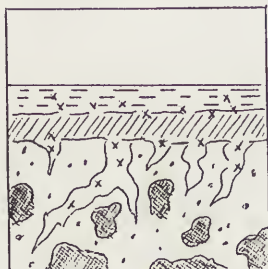
I - pack by ammonium carbonate (═ ═)-
Gypsum is converted into soluble ammonium sulphate (x ˣx) which is absorbed partly by pack and partly by plaster; calcium carbonate is produced;

- paint layer resets.

2 - pack by barium hydroxide (═ ═)-
remaining sulphate ions are converted into inert and insoluble barium sulphate (♦,♥);
excess barium hydroxide remains;

sulphatization is stopped.
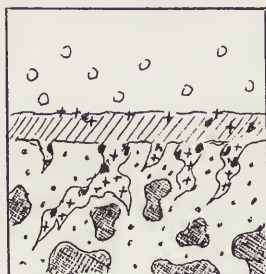
3 - atmospheric carbon dioxide (CO_2) slowly reacts with barium hydroxide; barium carbonate (✦✦✦) is produced which acts as a mineral consolidating agent;

cohesion is restored.

Fig.4 - Schematic steps of "Barium".

From this point of view barium carbonate is a mineral compound quite compatible with mural paintings and quite similar to calcium carbonate which is the major component of plaster. Its refractive index is such that it cannot falsify the characteristic optical reflectance of the paint surface nor the colours.

Moreover, after "barium", the painting may be subjected to any eventual future restorating operation with any agent dispersed in water or organic solvents as well.

"Barium" was applied with positive results also on paintings that were detached from the wall and transferred on a new support with calcium caseinate as an adhesive.

We must finally remember that while resin formulations are both consolidants and adhesive, "barium", being only a consolidant cannot work when macroscopic detachments (exfoliations etc.) are present.

It consolidates only incoherent microstructures.

With regard to this last point and considering the other properties, there should not be any obstacle to an extension of "barium" for the consolidation of other porous mineral materials.

It would prove to be, for example, an effective and appropriate agent to reestablish cohesion of degraded marble and stone antiquities.

Some preliminary tests in this context were already carried out (13). Further experiments are necessary but it is probable that also in this field "barium" may give   important and positive results.

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ISOLATION AND INVESTIGATION TECHNIQUES OF
MICROSCOPIC BIODESTROYER FUNGI DEVELOPING
ON FRESCO PAINTING AND OTHER MUSEUM OBJECTS

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SUMMARY

Herein there has been investigated a techni-
que of isolating biodestroyer micromycetes
from works of art. As a result of the inves-
tigation of damage to old Russian fresco pa-
inting and works of applied art it has been
established that in order to isolate the spe-
cies of paramount significance in the damage,
in addition to the standard media, it is ne-
cessary to use media whose composition must
corespond with the object damaged and the
specific conditions of the development of
biodestroyers in museums.
It is proposed that determination should be
made of the degree of "pathogenesis" for mu-
seum objects of microscopic fungi, isolated
from them, in accordance with their formation
of extracellular hydrolytic enzymes, organic
acids, pigments and physiological peculiari-
ties, such as their adaptation to the low
activity of water, and to entiseptics used in
the museum practice, and others.

Under certain conditions, microscopic fungi
can cause an irreparable damage to works of
art.
The extension of research into the field of
investigating the causes of the destruction
of painting, especially of fresco painting,
and other museum objects, made it possible to
establish that certain types of damage: pig-
mentation, peeling, loosening and loss of
connection with the base appear primarily
owing to the vital activity of micromycetes.
A diagram of the mycological analysis of works
of art and applied art (Fig. 1) was drawn ba-
sed on the generalization of our own experi-
ence and the analyses of the publications of
other authors (1-6).
Tinctured or white thin coatings, pigment
spots and various destructive changes are exa-
mined with a stereoscopic microscope, and the
most characteristic damage spots are photo-
graphed.
From these areas microbiological sowings are
made and microsamples are taken for a detail-
ed microscoping and for a biochemical deter-
mination of the metabolical activity level of
the fungi present in the sample under inves-
tigation. During the process of investigating
the damage caused by fungi, good results are
obtained by using scanning electron micro -
scopy. Thanks to the greet depth of the focus
and high resolution it is possible to observe
smallest spores and hyphae of micromycetes
right on the surface of the material under
investigation, and simultaneously, the speci-
fic features of its destruction.
When isolating cultures of biodestroyer mic-
romycetes depending on the kind of a work of
art and on the degree of the development of
the damage, sowings are used according to the
technique of dry needle, washing with a tam-
pon, or placing small samples of the damaged
material on dense mineral media.

In order to determine the number of fungi in
the sample, suspension is made aither from
a weight of the material under investigation,
or from the tampon, with which the sample was
taken and which is washed with water contain-
in twin. In both cases, after multiple dilu-
tions of the basic solution, sowings are made
on petri dished with subsequent calculation
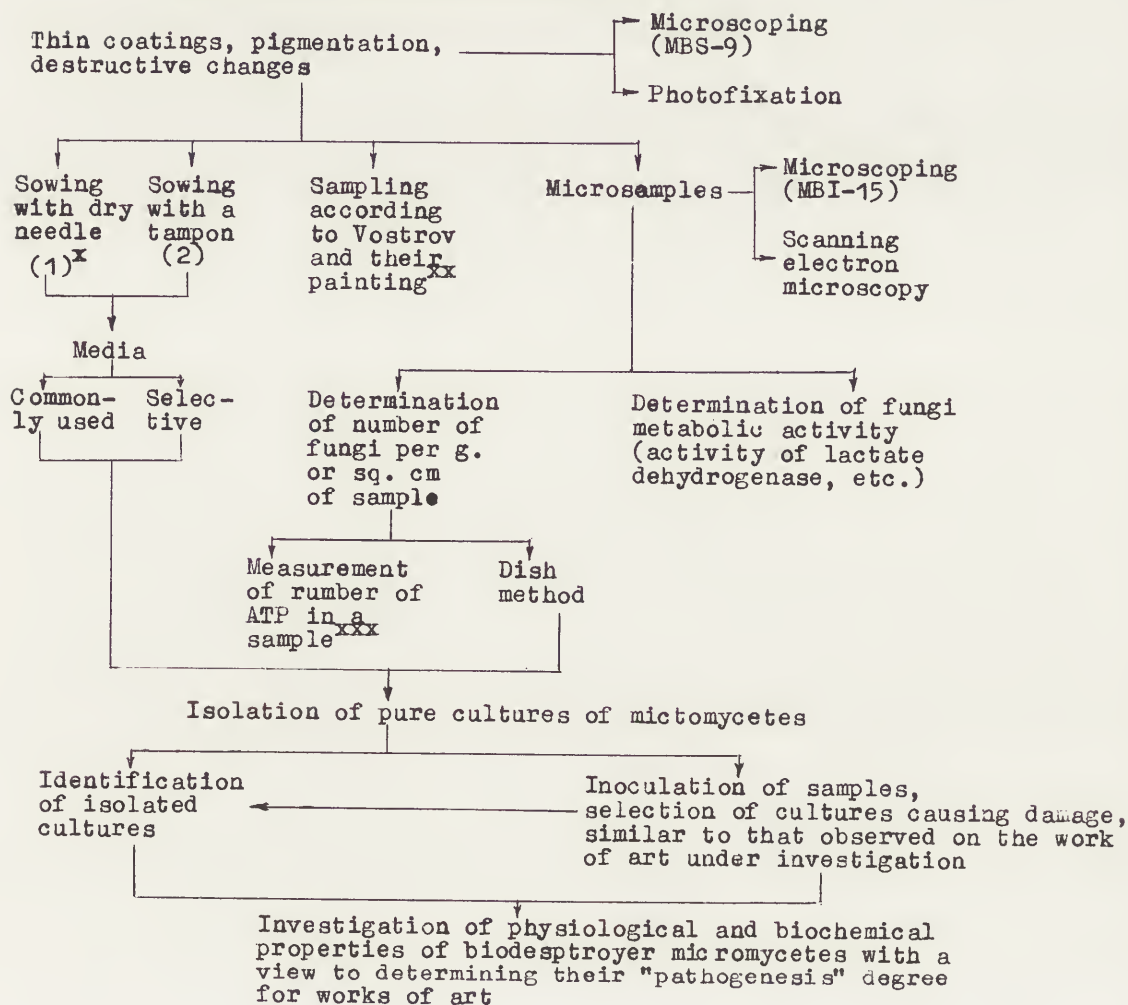of the number of fungous colonies that deve-
loped.
Developing on works of art, micromycetes are
frequently placed in the extreme conditions
of their existence, determined by such envi-
eonment factors as low activity of water, low
temperature in unheated premises, the presen-
ce of compounds of heavy metals which are
constituents of pigments, and in some cases,
small amount of organic matter. However, owing
to their high adaptability, fungi adapt to
such conditions that should be taken into ac-
count when isolating them on artificial nut-
rient media.
The traditional dense nutrient media for the
isolation of soil and biodestreyer fungi,
malt-agar and Chhapek agar, contain carbohyd-
rates accessible to many fungi, and have high
water activity (0,98-0.99). On such media
fast growing species of the ecological group
of the so-called "sugar" species fungi some-
times impede the development of micromycetes
of genuine significance to the damage. There-
fore, to reveal the fungi forms playing a
fuctional role in the destruction, as di-
stinct from epiphytic forms, accounting for
the general spore overgrowth of the object,
in addition to the standard media, it is ne-
cessary to use media whose composition cor-
responds with feeding requirements of bio-
destryers and environment conditions in which
they develop (pH, low water activity, lack of
organic matter).
When analysing the damage to old Russian fres-
co painting, positive results were obtained
in the isolation of specialized fungi forms
on the "lime" agar (agar - 2%, powdered plas-
ter - 10%). Virtually pure cultures of dark
coloured fungi, requiring very slight amount
of organic matter, were isolated on the "li-
me" agar from the fresco paintings (17th cen-
tury) of the Church of John the Theologian
in Rostov Veliky. The majority of isolated
cultures were determined as Cladosporium
sphaerospermum. The revelation of adapted fun-
gi forms is facilitated also by the use of
"hunger" agar containing the mineral part of
the Chapek agar + 0.1% of saccharose, and
0.6% of Balling agar, malt-agar with low wa-
ter activity, as well as media selected by
the source of carbon.
The isolation of micromycetes on nutrient me-
dia makes it possible to reveal the set of
species present in the damage area, and to de-
termine its spore overgrowth. This method is
not always capable of giving an idea of the
condition of mictomycetes, in spore condi-
tion or actively growing mycelium. Micromy-
cetes are stable against the effect of many
environment factors unfavourable for their
development; under the conditions when fungi
vital activity is impossible, they transform
into dormance (spores) retaining vital capa-
city for a long period of time. It is possib-
le to determine which condition fungi, pre-
sent on works of art, are in, by employing
biochemical tests, for instance, according to
the activity level of glycolysis enzymes, or
by biophysical methods.
The investigation of physiological and bio-
chemical properties of fungi isolated from mu-
seum objects is aimed at revealing "pathoge-
nesis" factors. These are, above all, the
presence of hydrolytic and oxidizing enzymes
in the cultures under examination, the forma-
tion of organic acids by them, pigment forma-
tion, zerophily and others. The study of phy-
siological and biochemical properties of fun-
gi makes it possible not only to understand

Fig. 1

Mycological Analysis of Works of Art

Thin coatings, pigmentation, ────── ┌─ Microscoping
destructive changes   │ (MBS-9)
                                       └─ Photofixation

Sowing   Sowing   Sampling   Microsamples ─ ┌─ Microscoping
with dry   with a   according   │ (MBI-15)
needle   tampon   to Vostrov   └─ Scanning
(1)[x]   (2)   and their   electron
                            painting[xx]   microscopy

        Media

Common-   Selec-   Determination   Determination of fungi
ly used   tive   of number of   metabolic activity
                     fungi per g.   (activity of lactate
                     or sq. cm   dehydrogenase, etc.)
                     of sample

                Measurement   Dish
                of number of   method
                ATP in a
                sample[xxx]

        Isolation of pure cultures of mictomycetes

Identification   Inoculation of samples,
of isolated   ◄───────   selection of cultures causing damage,
cultures   similar to that observed on the work
                                  of art under investigation

        Investigation of physiological and biochemical
        properties of biodesptroyer micromycetes with a
        view to determining their "pathogenesis" degree
        for works of art

[x] 1 or 2 are employed depending apon the degree of micromycetes development
[xx] constitution of the dyestuff: phenol – 2 g, lactic acid – 2 ml, glycerine – 1 ml, water – 2 ml, cotton blueing 4Bor Y4B – 0.2-1.%, dyeing period – 10 minutes; the size of a Scotch tape band is less than 10 sq. cm.

[xxx] the technique is based on the absence of adenosine triphosphate in the substrate, it is applicable if the number of cells is more than 10^4 per g of sample.

the destruction mechanism of works of art, but also to use the information obtained to work out effective and safe method of suppression of biodestroyers.

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Section 16

Coatings: Evaluation and
Characterization

Couches: Evaluation et
caractérisation

COATINGS: EVALUATION AND CHARACTERIZATION

Coordinator   : E. De Witte (Belgium)
Assistant coordinator: N.H. Tennent (UK)
Members: R.L. Feller (USA)
        N. Baer (USA)
        H. Burgess (Canada)
        Ch. Costain (Canada)
        A. Diethelm (Switserland)
        J. Down (Canada)
        D. Dwyer (USA)
        F. Flieder (France)
        S. Florquin (Belgium)
        E. Jordan (USA)
        R. Lafontaine (Canada)
        S. Lee (UK)
        I. Nazarova (USSR)
        G. Nelson (USA)
        T. Nishiura (Japan)
        L. Masschelein-Kleiner (Belgium)
        W. Mourey (France)
        J. Petit (France)
        F. Piacenti (Italy)
        F. Preusser (USA)
        W. Roelofs (The Netherlands)
        M. Sawada (Japan)
        J.H. Stoner (USA)
        L. Van Zelst (USA)
        Ph. Weil (USA)
        R. White (UK)
        S. Williams (Canada)

At the 6th triennial meeting in Ottawa two
candidates were proposed as assistant
coordinator: Dr. N.H. Tennent and Dr. R.
Lafontaine. In February 1982 a voting ballot
was send to the members. Most of them replied
promptly and it was Dr. Tennent who has been
elected. In August of the same year a
questionnaire, asking for specific needs and
information was send. About 50% of the
members replied. The general line was that
there exists a need for chemical analysis
used as coatings. A programme in that sense
was set up and will be discussed. At the same
time the assistant coordinator will propose
an interlaboratory comparision of light-
fading apparatus in use for testing conserva-
tion materials.

The complete programme can be summerized as
follows:
1. Characterization of synthetic resins used
   in conservation. An exact identification
   of these resins is necessary to allow
   the conservator to know the products
   he is using and to allow him to replace
   a product, which is not available in his
   country, by a chemical identical product.
2. Identification of natural resins used as
   coatings. This includes also the charac-
   terization of the degradation products.
3. To provide testing and ageing methods
   to collegues of other working groups
   so that everyone can rely on the same,
   comparative tests.
4. To examine the properties of new resins
   and their possibilities as protective
   coatings for works of art, ethnographical
   and archaeological materials.

EXPERIMENTAL STUDY ON THE ADHESION STRENGTH OF LACQUER COATING

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1 Test specimens

Test specimens were five lacquered wooden boards(40 x 15 x 1.5 cm) which were coated respectively by five specialists in lacquer coating. They were coated according to the procedure shown in Table 1. Each stage of the procedure was applied in the numbered order, leaving a space to show the preceding stages, so that the support wood(W) and layers(①~⑩) were exposed successively as shown in Fig.1. In this paper, the five specimens are called A, B, C, D and E for convenience. Each specimen was cut into eight test pieces as shown in Fig.2.

Summary

Adhesion strength of lacquer coating was experimentally examined by means of a vertical tension test, using test specimens which were made according to a specified procedure by five specialists in lacquer coating. In order to examine the stability in strength, the specimens were tested under four conditions: normal state, after deterioration treatment by hot water, by boiling, and exposure in the open. As results; i) Adhesion strength and its stability , especially its weathering property, of the lacquer coating was greatly dependent on the person who applied the coating. ii) However, the weakest and the next weakest layers of the coating of every specimen were the nuno-gise(appling cloth) layer and urushi-shitaji(foundation Ⅲ)layer. From the results, it can be considered a general characteristic of lacquer coating that the nuno-gise layer and urushi-shitaji layer are the weak points. Nuno-gise technique is so complicated that it is impossible to discuss the way of its improvement here. Urushi-shitaji layer can be strengthened by increasing the amount of the lacquer added to the filler of tonoko.
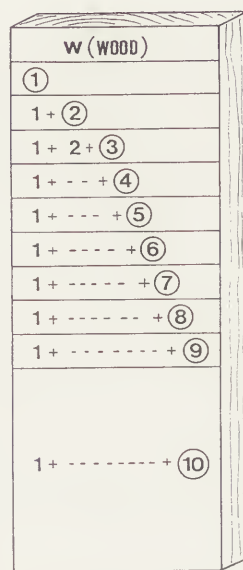
Fig.1 Lacquered test specimen
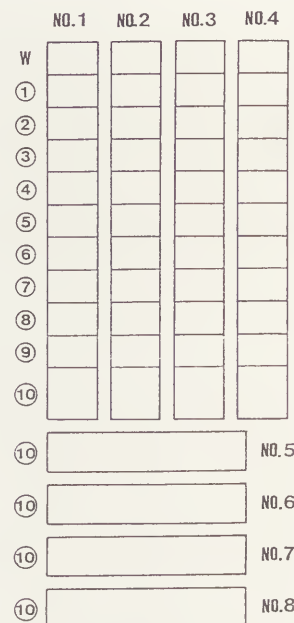
Fig.2 Test pieces cut from the specimen

Table 1. Method of lacquer coating of test specimen

	Successive layers	Material	Polishing
①	Kiji-gatame (Sealing of support wood)	Ki-urushi(raw lacquer)	
②	Nuno-gise (Appling cloth)	Hemp or cotton cloth with mugi-urushi(mixture of raw lacquer and flour)	
③	Nunome-suri (Filling texture of cloth)	Mixture of raw lacquer and jinoko(rough clay powder)	Kara-togi (Whetstone without water)
④	Urushi-jinoko (Foundation I)	ditto	ditto
⑤	Kiriko (Foundation Ⅱ)	Mixture of raw lacquer and jinoko and tonoko(fine clay powder)	ditto
⑥	Urushi-shitaji or Sabi (Foundation Ⅲ)	Mixture of raw lacquer and tonoko	Mizu-togi (Whetstone with water)
⑦	Sabi-gatame (Consolidation of foundation Ⅲ)	Raw lacquer	
⑧	Shita-nuri (Under coating)	Roiro-urushi(black lacquer)	Sumi-togi (Charcoal with water)
⑨	Naka-nuri (Middle coating)	ditto	ditto
⑩	Uwa-nuri (Top coating)	ditto	

2 Test method

An iron jig, with 2 × 2 cm section, was glued to the surface of each test piece with an epoxy adhesive, and the lacquer coating was cut down to the support wood along the rim of the jig, as shown in Fig.3[A][B]. Then each test piece was set to a tension testing machine, and was subjected to a vertical tensile load untill the lacquer coating or the support wood was broken(Fig.3[B][C][D]). The broken layer was recorded, and the vertical tensile strength was calculated from the maximum tensile load according to the following equation:

$$T = \frac{P}{S} = \frac{P}{4}$$

T; Vertical tensile strength(kg/cm^2)
P; Maximum tensile load(kg)
S; Square measure of the broken area(4cm^2)

2.1 The test of each layer of the coating

Each layer(① ~ ⑩) of the coating was examined by a vertical tension test, using the test pieces No.1-4(Fig.2) of the specimens A-E. The purpose of this test was to know clearly the weakest layer of the lacquer coating of the specimens.

2.2 Repeating test after fixing the broken parts

Vertical tension test was done with the test pieces No.5-8(Fig.2) of each specimens. After that, the broken parts were fixed by gluing with an epoxy adhesive. Then, the test was done again. This procedure was repeated untill breaking occured in the support wood. The purpose of this test was to know the layers which were weaker than the support wood, in the order of their weakness. In order to examine the stability of the lacquer coating in strength, this test was done under the following four conditions:

1) Normal state(test piece No.5)
2) After deterioration treatment with hot water(test piece No.6)
   Test pieces were immersed in 70°C water for 2 hours, then dried in an oven at 60°C for 3 hours.
3) After deterioration treatment by boiling (test piece No.7)
   Test pieces were boiled in water for 4 hours, then dried in an oven at 105°C for 20 hours. The test pieces were subjected to two cycles of this procedure.
4) After deterioration treatment by exposing in the open
   Test pieces were exposed in the open on the roof of the institute for 16 months including two summers(Jun., 1979 - Oct., 1980)

3 Test results

3.1 The test of each layer of the coating

The results are shown in Fig.4. In Fig.4, ① - ⑩ show the successive stages of the coating (Table 1, Fig.2,3), dotted lines represent the

【A】

【B】

GLUED BY EPOXY

LACQER LAYER

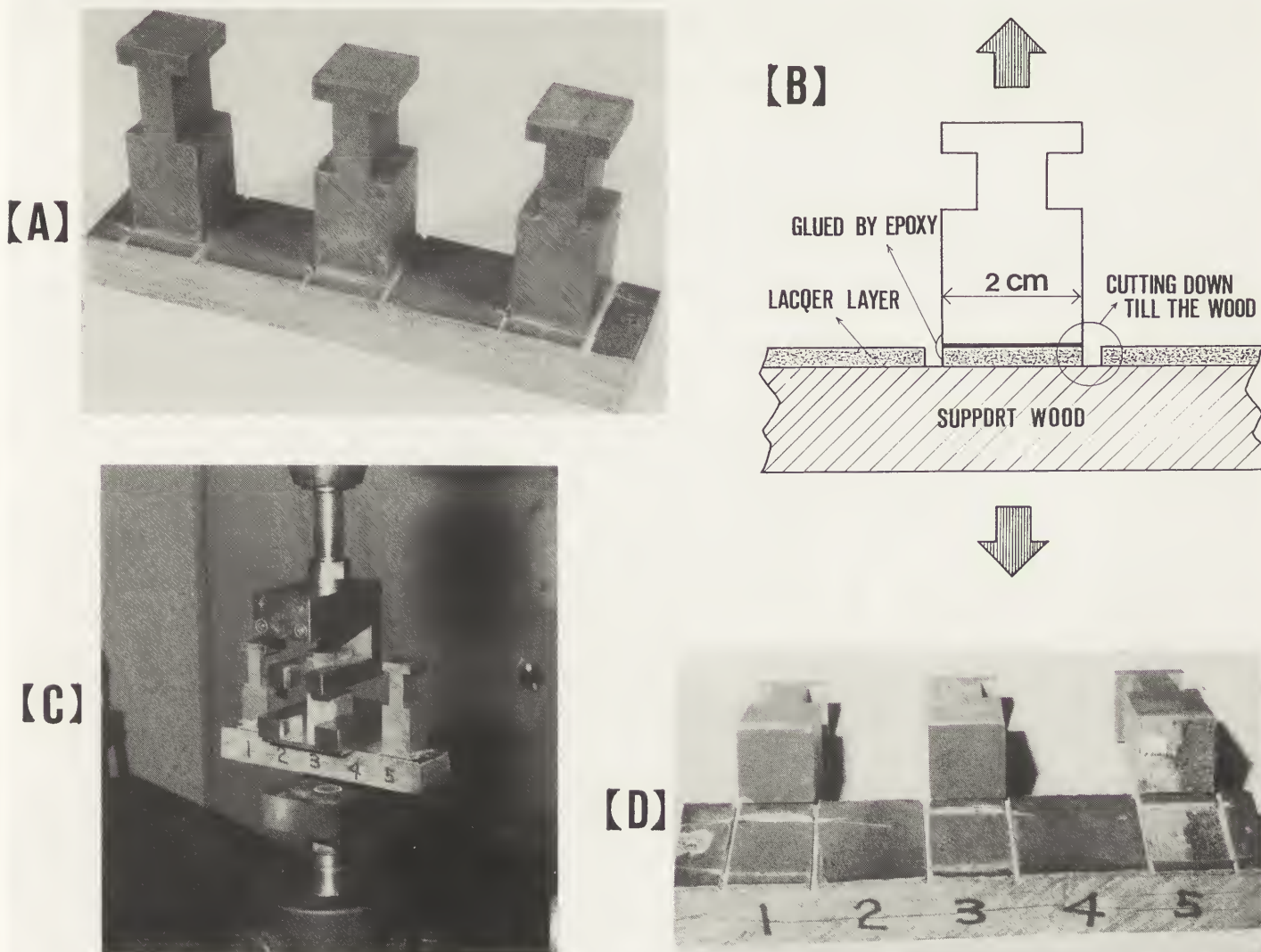2 cm

CUTTING DOWN TILL THE WOOD

SUPPORT WOOD

【C】

【D】

Fig.3   Way of vertical tension test

broken layers and upper graph shows the vertical tensile strength(dotted line is the standard deviation). Each data is the mean of the four test pieces.

In case of A, obviously the nuno-gise(clothing) layer[②] is the weakest, and its strength is considerably low. In case of B, ② is also the weakest layer in comparison, but its strength is quite high, so ② is not necessarily the weak layer. In case of C, urushi-shitaji(foundation Ⅲ)[⑥] is the weakest layer in comparison, but it is not the significant weak layer considering its quite high strength. In case of D, ② may be the weakest layer in comparison, but it is never the weak layer considering the fact that its strength is high and that the breaking occured in the support wood. In case of E, obviously ⑥ is the weakest layer with its low strength.
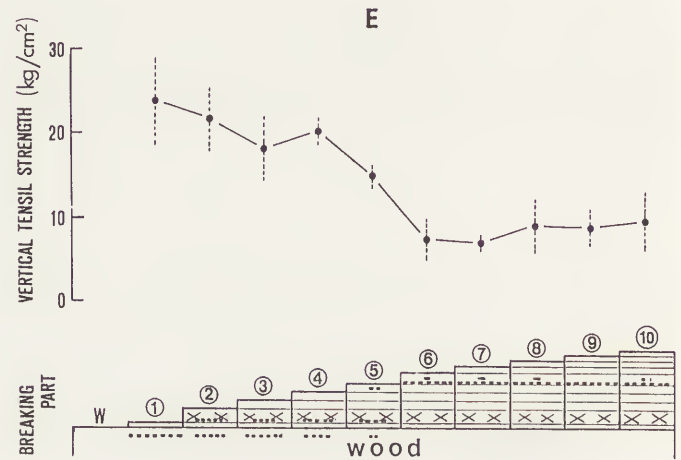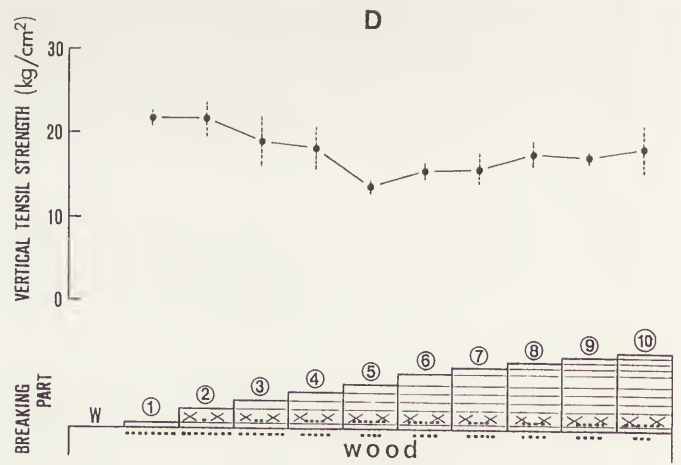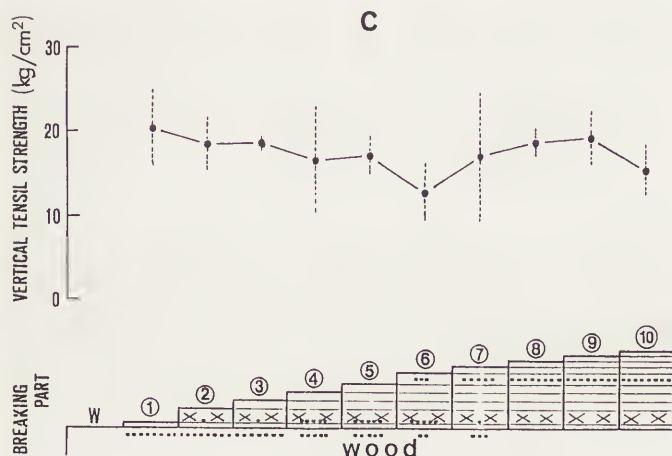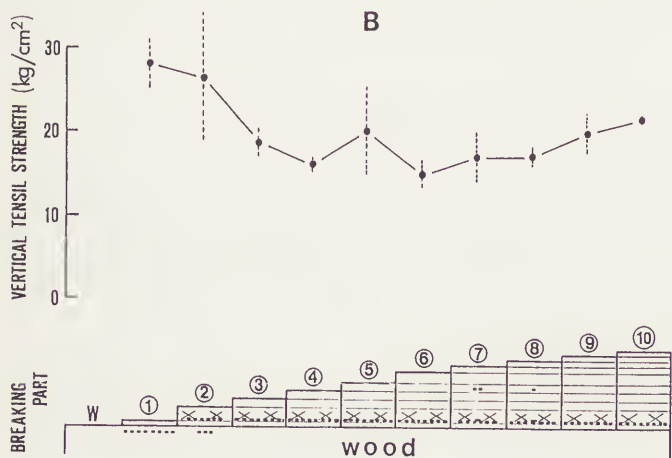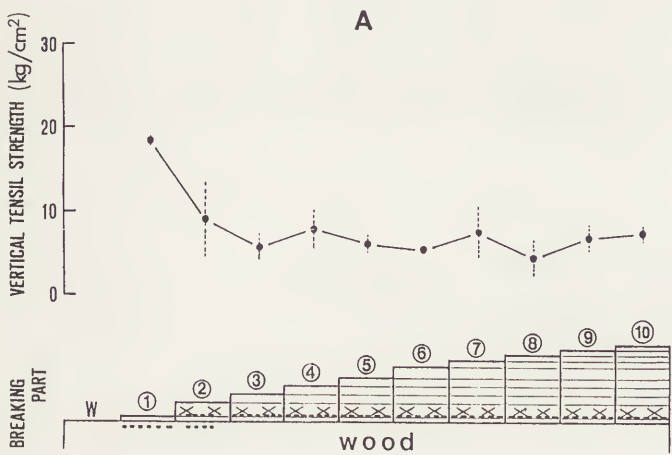
Fig.4 Vertical tensile strength and the broken layer by the test of each layer of coating

3.2 Repeating test after fixing the broken parts

Test results of the four conditions are shown in Fig.5-8 respectively. In the figures, lower numbers indicate the numbers of the tests(1st, 2nd, -----), dotted lines represent the broken part at each test, thick straight lines represent the fixed parts and upper graph is the vertical tensile strength(dotted lines is the standared deviation). Each data is the mean of the five places of each test piece.

1) Normal state

Fig.5 shows the results. In case of A, nuno-gise[②] with its low strength is the weakest layer. But, urushi-shitaji[⑥] is almost as weak as ② . In case of B, ② is the weakest and ⑤ may be the next in comparison. But, their strengths are very high and almost the same as the support wood. The lacquer coating is considered very good. In case of C, ⑥ is the weakest layer and ② is the next. But their strengths are very high, so that it is not right to consider these two layers as weak. In case of D, ② may be the weakest layer in comparison. But, the lacquer coating should be considered good, by the fact that its strength is quite high and the breaking occured in the support wood even in the first test. In case of E, the weakest layer is ⑥ and its strength is lower than the others'. The reason for the low strength values after the second may be that the inner breakings were left even after the fixing because of the complex breaking by the second test.
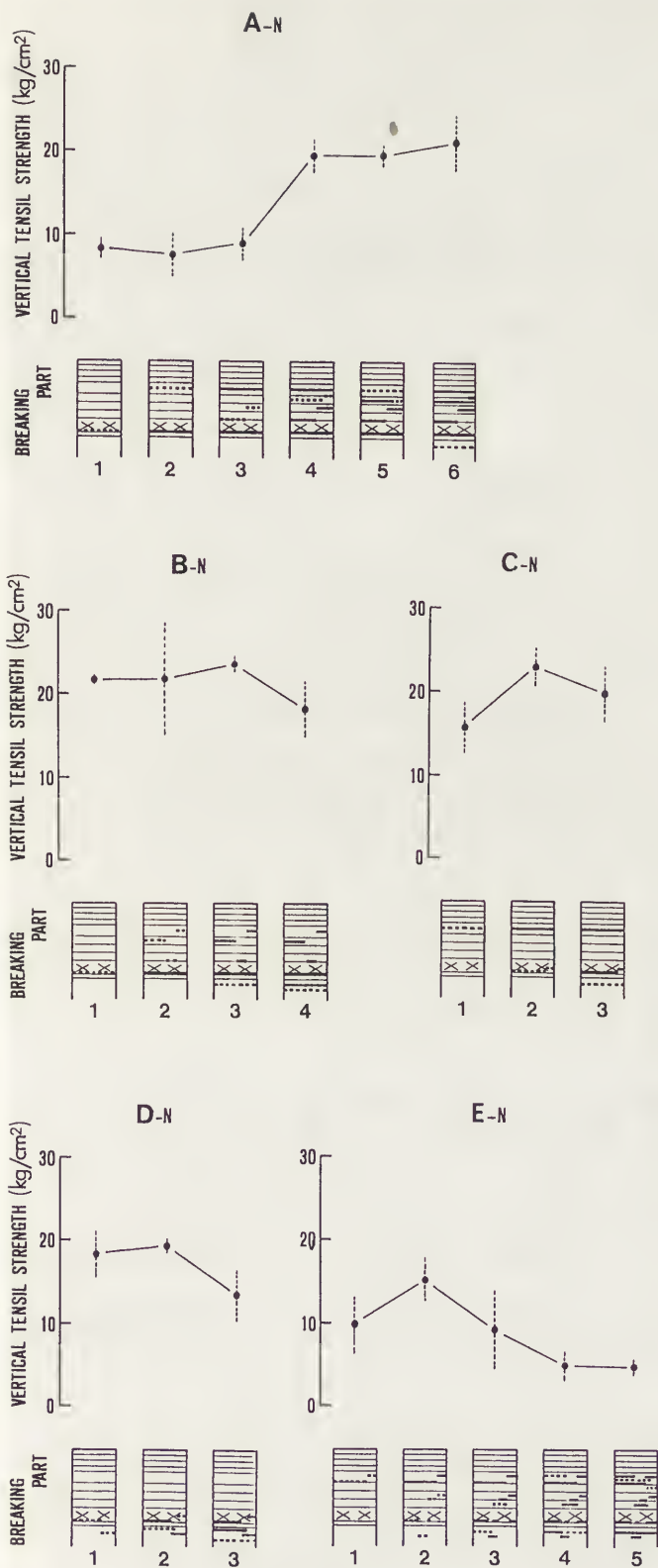
Fig.5 Vertical tensile strength and the broken layer by the repeating tests after fixing the part which was broken by the just previous test [normal state]

2) After deterioration treatment with hot water

Fig.6 shows the test results. In general, the strength of the lacquer coating was not affected by this deterioration treatment. The behavior in strength of the specimens were almost the same as in normal state. However, some peculiar changes were found. In case of A, urushi-shitaji[⑥] increased its strength more than two times, and, in case of B, it also obviously increased its strength. On the

contrary, in case of E, it significantly decreased its strength.
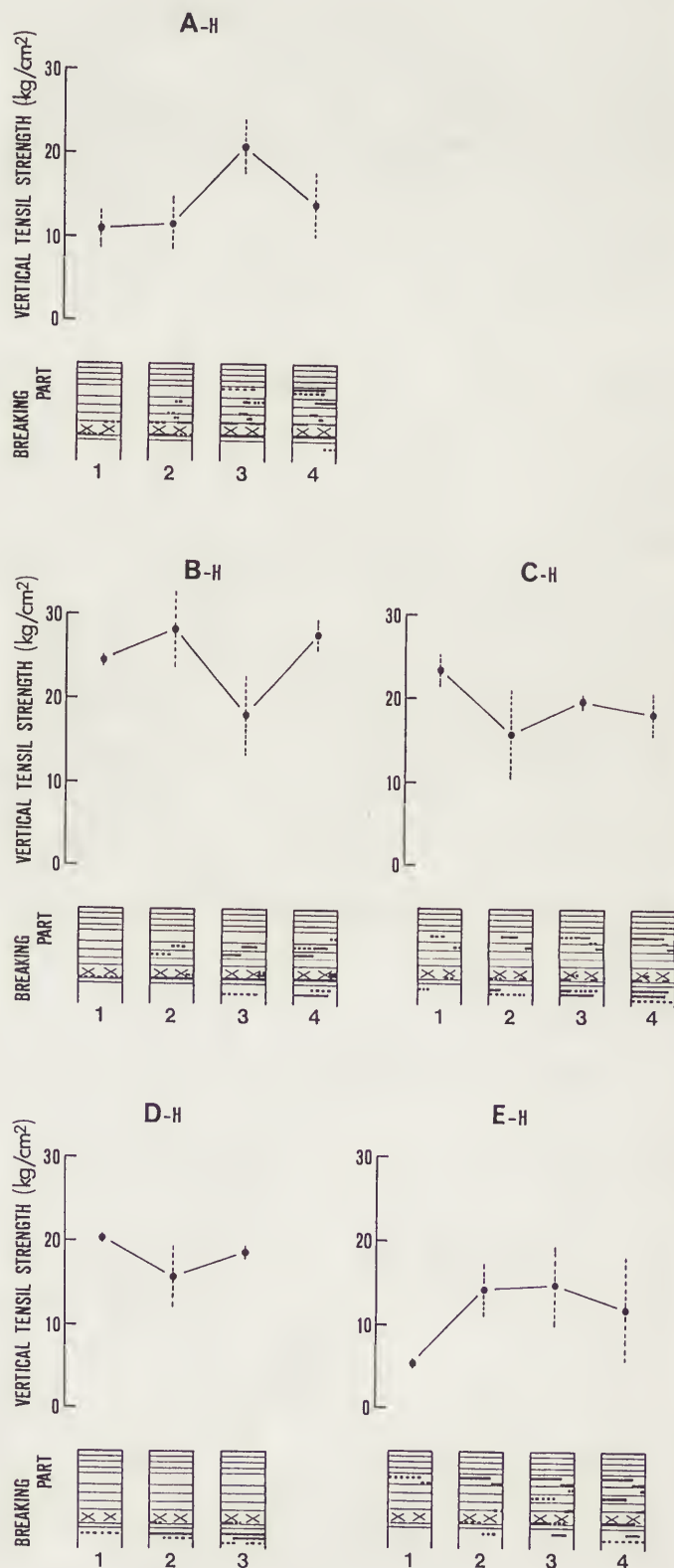
Fig.6 Same as Fig.5, but, [after deterioration treatment with hot water]

3) After deterioration treatment by boiling

Fig.7 shows the test results. In case of A, the strength of ② , which was still the weakest layer, did not change. But, the other layers were weakened and their strengths became almost as weak as ② . In case of B, on the contrary, ② was greatly weakened to be obviously the weakest layer. But the other layers were still in good condition. In case

of C, ⑥ became the weakest layer in comparison instead of ②. But all the layers kept high strength. In case of D, the behavior in strength was almost the same as the one in normal state which was good. The measured strength value of the second test was very low, most probably because the inner breakings were left in the support wood by the first test. In case of E, ②, which was in good condition in normal state and after the deterioration treatment with hot water, was greatly deteriorated, and its strength became 0. ⑥ was also very weakened to have only a very little strength. The low measured strength values of the 4th and 5th tests are considered to be caused by the residue of the inner breaking by the complex breaking at the 3rd test.
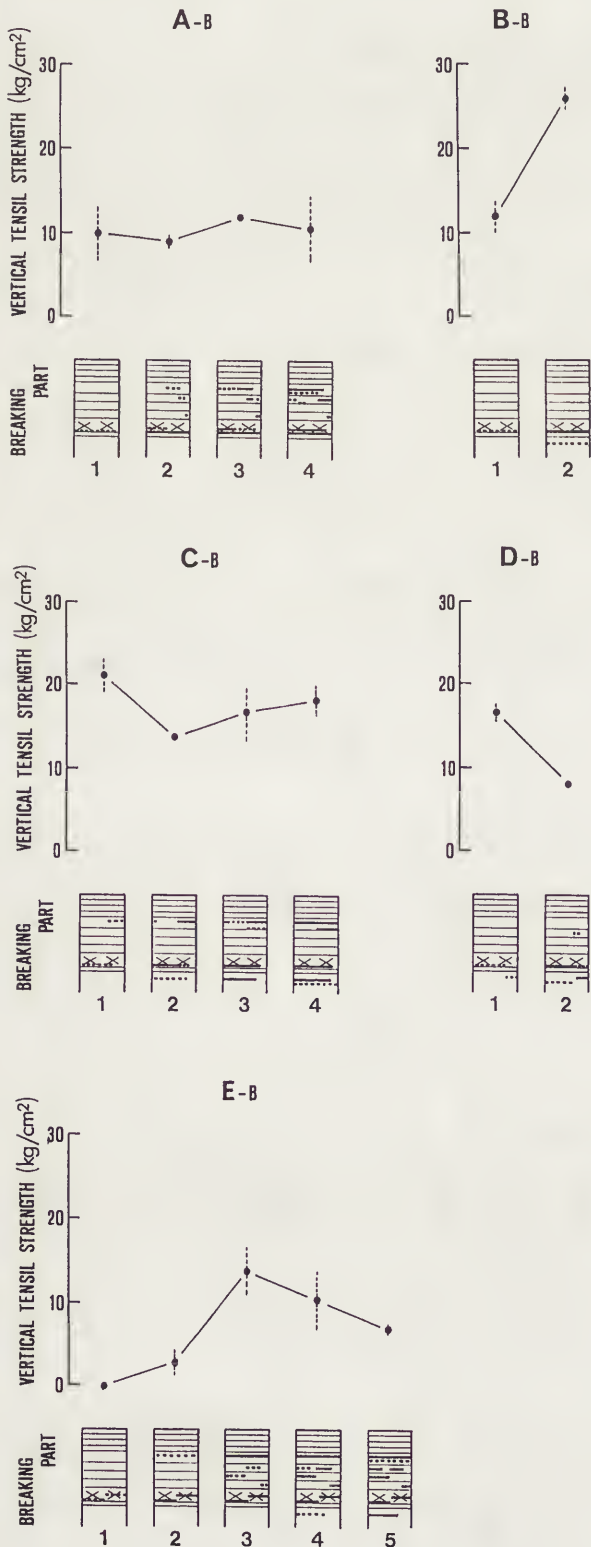
4) After deterioration treatment by exposing in the open

Fig.8 shows the test results. In case of A, the lacquer coating had already been divided into two parts from layer ② before the test. So, the strength was 0, of course. However, ⑥, which was as weak as ② in normal state and after the deterioration treatment with hot water, deteriorated a little in strength. B showed the same tendency as A. ② greatly deteriorated, reducing its strength to be lower than one fourth of the normal state. But, the other layers deteriorated little in strength. In case of C, although ⑥ deteriorated considerably, reducing its strength to be 50% of the one in normal state, the value of the strength was still not so low. The other layers were still in good condition in strength. The reduced strength values measured at the 3rd and 4th tests are considered to be due to the residual inner breaking in the support wood. D showed little deterioration. It was in good condition. The reduced strength value measured at the 2nd test is considered to be due to the residual inner breaking in the support wood. E showed a peculiar behavior that the lacquer coating increased its strength instead of deteriorating. Since, at the first test, the breaking occured in the support wood, the real strength of ⑥, which was the weakest layer, had to be higher than the measured value. Therefore, this increasing of strength should be considered significant. The reason for the reduced strength value measured at the 2nd test is considered to be the same as C and D.
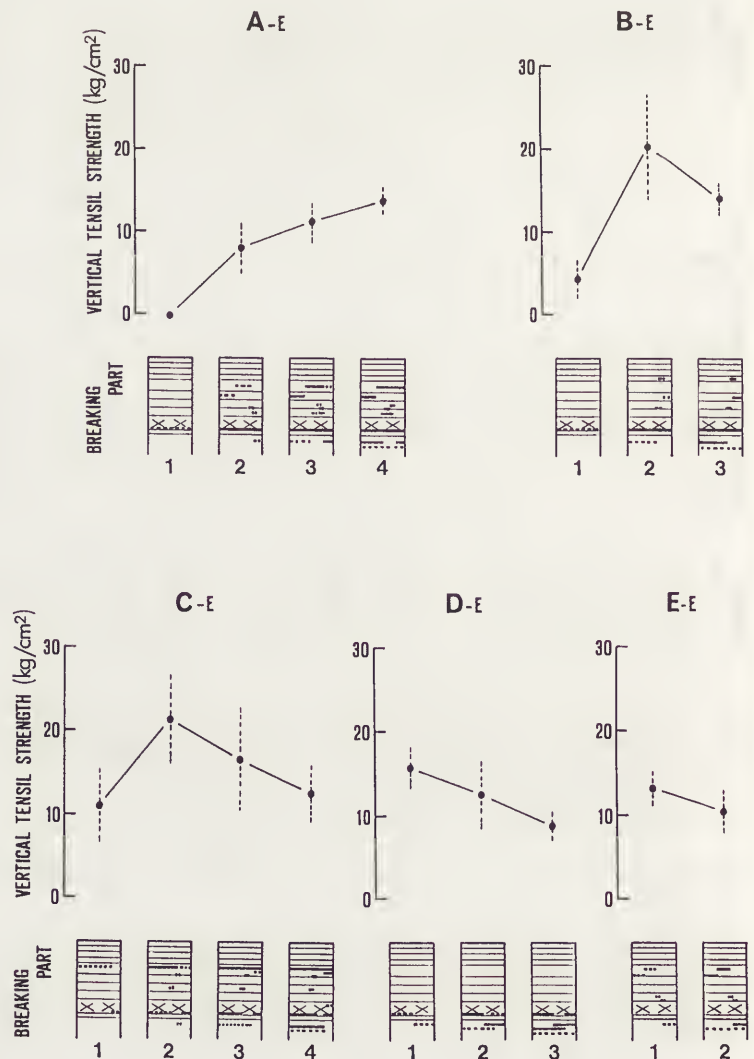

Fig.7 Same as Fig.5, but, [after deterioration treatment by boiling]

Fig.8 Same as Fig.5, but, [after 16 months' exposure in the open]

4 Discussion

Lacquer technique is specially traditional. It is not standarized unlike modern technology, although it has been highly developed individually. Therefore, it is generally supposed that the characteristics of the lacquer coating is different depending on the person who applied it. This supposition is confirmed by the test results that the five lacquered test specimens were significantly different from one another in their characteristic of vertical tensile strength and its stability.

On the other hand, however, a property common to the five specimens was found by the test. It is that the weakest layer in the lacquer coating is either nuno-gise layer or urushi-shitaji layer, and the next weakest layer is also either of the two layers. In other words, when nuno-gise is the weakest, urushi-shitaji is the next weakest, and when urushi-shitaji is the weakest, nuno-gise is the next weakest. In short, nuno-gise layer and urushi-shitaji layer are the weak points of the lacquer coating. This property can be considered a general characteristic of lacquer coating, considering the test results that the property was common to all the specimens while their strengths were different from one another.

Nuno-gise is attaching a hemp(sometimes cotton) cloth on the support wood which has been sealed with raw lacquer(kiji-gatame) beforehand. There are two manners of attaching the cloth. One is to daub mugi-urushi(mixture of raw lacquer and flour) on the support then to put a cloth on the support and to press it. The other one is to daub mugi-urushi to a cloth then to put the cloth on the support and to press it. In the former case, the "intimacy" between the cloth and mugi-urushi is apt to be insufficient, and consequently the adhesion between them can be diminished. In the latter case, the total contact area between the mugi-urushi and the support decreases as shown in Fig.9, so the total adhesion strength decreases. It is to be regreted that the relationship between the test results and the manner of the nuno-gise for the test specimens can not be discussed here. It is very difficult for the author to know by which manner the nuno-gise of the test specimens were done because it is in a way the specialists' individual secret. Thickness of the yarn and texture of the cloth are also important factors for the property of nuno-gise layer. And, the drying condition is very important especially for nuno-gise, because significantly large amount of lacquer is applied to this layer. Thus, nuno-gise layer is very complicated to study. So, systematic experiments only on nuno-gise layer are necessary for futher study.

The weakness of urushi-shitaji layer can be considered to be due to the insufficient amount of lacquer contained in the layer. The techniques of ④ nunome-suri[filler; jinoko (rough clay powder)], ⑤ kiriko[filler; 1:1 mixture of jinoko and tonoko(fine clay powder)] and ⑥ urushi-shitaji[filler; tonoko] are the same. First the filler is mixed with water and kneaded to a certain softness. After that, the mixture is mixed with raw lacquer and kneaded and then daubed by a spatula. Here, attention should be payed to the size of powder of the fillers. Tonoko is much finer than jinoko, which means the balk density and the surface space of tonoko are much higher than jinoko. Therefore, to get a certain degree of cohesion, a larger amount of raw lacquer than jinoko or kiriko has to be added to tonoko. Practically, however, almost the same amount of raw lacquer seems to be added to the three kinds of filler. Thus, the relative amount of lacquer for the filler of tonoko may be smaller than for the other fillers. Consequently, the cohesion of urushi-shitaji may be lower than the other layers except nuno-gise layer. The strength and its stability of urushi-shitaji, therefore, could be improved by increasing the amount of raw lacquer added. ⑦ kiji-gatame may be translated 'consolidation of foundationⅢ (urushi-shitaji)' in English. Actually, however, it is not for the consolidation of urushi-shitaji but the pretreatment of the surface of urushi-shitaji for the subsequent coatings ⑧ - ⑩. So, essentially it makes no contribution to the reinforcement of urushi-shitaji. The results of the test before and after the deterioration treatments are shown in the lump in Fig.10. In Fig.10, [A] - [E] represent the specimens, numbers in circles indicate the broken layers, N means test in normal state, H after the deterioration treatment with hot water, B after the deterioration treatment by boiling and E after exposing in the open. As clearly shown in Fig.10, the characteristic of E is very peculiar. The strength after the exposure in the open is higher than before the exposure, which can not be normaly understood. And, the strength of E is reduced 50% after the treatment with hot water and reduced to zero after the treatment by boiling, while the strengths of the other four specimens increased a bit after the treatment with hot water and did not reduce so much after the treatment by boiling. To understand this special behavior of specimen E, the fact that it was made later than the other four specimens because of the circumstances of the specialist who made it, should be considered. The time between the completion of the specimen E and the testing was quite short in comparison with the other four specimens. In general three dimensional plastic, including lacquer, has a very high durability against water. But, in the stage of its insufficient hardening, it does not have resistance to water at all. So, the peculiar action of the specimen E could be explained by the supposition that it had not yet hardened sufficiently when it was tested in normal state, after the treatment with hot water and after the treatment by boiling, but it hardened sufficiently during the duration of 16 months' exposure in the open. Futher experimental study on hardening action of lacquer should be necessary to discuss the propriety of this supposition.

Thus, here, it seems to be proper to discuss the test results of the other four specimens. All four specimens increased their strengths by the treatment with hot water instead of deteriorating. This phenomenon can be explained by the hardening characteristic of the three dimensional plastic including lacquer, that is, it hardens gradually little by little with time even after sufficient hardening. The gradual hardening after sufficient hardening of the lacquer coating of the specimens A - D which were quite young, might have been accelerated by the treatment with hot water. This hardening action of the specimens A - D is completely different from the action of the specimen E
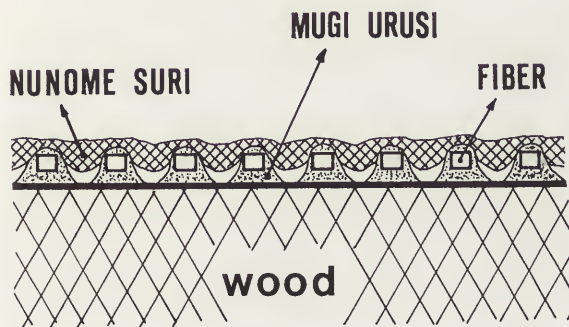

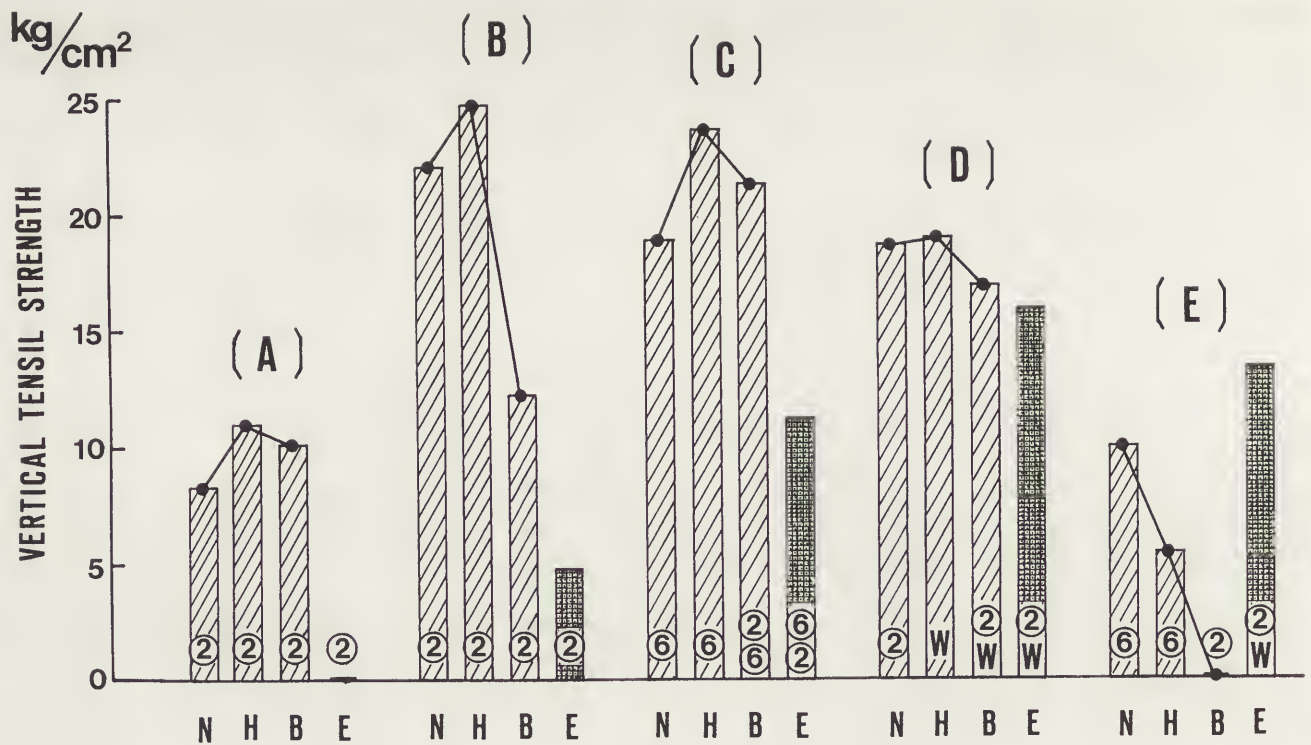Fig.9 Illustration of the section of nuno-gise layer

Fig.10 Vertical tensile strength and the broken layer of the five test specimens
under the four conditions

mentioned above. The boiling-drying cycles is very severe treatment to deteriorate a coating in order to test the durability against water attack. A, C and D were little deteriorated by this treatment. B was deteriorated and the strength reduced 50%, but the strength value was still sufficiently high. From these results, it can be said that the lacquer coating has very high durability against water attack.

As for the deterioration by the exposure in the open, There were big differences among the specimens. The lacquer coating of A had divided into two parts from the nuno-gise layer before the tension test. B extremely reduced its strength down to 5 kg/cm^2 which is 1/4 of the strength in normal state. On the contrary, D deteriorated only a little bit. C lost 40% of its strength, but the value was still sufficiently high. A and B were extremely deteriorated by the treatment of exposing in the open in this experiment. However, this fact does not directly mean that, if A or B were a real exterior coating on a building, it would deteriorate to the same extent as the test result, because the exposing condition for this experiment is considered much more severe than the natural condition in which actual buildings are normaly subjected to, by the following aspects:

i) The ends and sides and back of the specimen were not covered, so that the section of the lacquer coating was directly exposed.

ii) The test piece was small and long perpendicular to the fiber of the support wood, so that the lacquer coating suffered greatly from the dimensional change of the support wood.

Therefore, the test of exposure in the open of this experiment should be considered one of the accelerated weathering tests by which the test specimens are just compared from one another. In comparison, D has an excellent resistance to weathering, and C is also quite good. On the contrary, A and B have very poor resistance to weathering. As for E, though the problem of its hardening mentioned above has

to be taken into account, the test result was quite good. It can easily be understood that it is impossible to discuss here the reason of the differences in weathering action among the specimens only with the test results of this experiment. Much futher study is necessary to find out even a clue, because the lacquer technique is extremely traditional and it is sometimes misterious.

At the end, though it is too obvious to state, the author would like to confirm that he will never and can never make a remark on the quality of the techniques of the persons who made the specimens.

5 Acknowlegement

THE PHOTOFADING OF DYESTUFFS IN EPOXY, POLYESTER AND ACRYLIC RESINS

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SUMMARY

The accelerated light ageing of fourteen dyestuffs dissolved in epoxy (Ablebond 342-1), polyester (Metset SW) and acrylic (Plastogen G) resins has been studied. The dyes show good light stability in acrylic medium but more dramatic photofading in polyester and epoxy resins. The colour changes, measured instrumentally and plotted in CIELAB colour space, indicate that fading is accompanied by a change in hue in certain cases. The undyed acrylic resin yellows more than the epoxy and polyester resins, but certain dyes stabilise the acrylic substrate against yellowing. On the other hand, for some dyed epoxy resin casts, the degradation and yellowing of the resin is accelerated compared to the undyed samples. Considerable recovery of colour on dark storage after light ageing is a significant feature of the behaviour of four of the dyes. These observations demonstrate the inadvisability of using dyed polymers for conservation without first testing the lightfastness of the dye/resin combination.

1. INTRODUCTION

Many branches of conservation require the use of coloured polymer coatings of good lightfastness; in the restoration of ceramics (1) and stained glass (2), for example, dyed and pigmented polymers are used both as casting resins for gap filling and as coatings for retouching. It is well established that, since the lightfastness of a dyestuff depends on the medium in which it is incorporated, it is meaningless to specify its lightfastness without reference to the substrate. The work reported in this paper forms part of an ongoing investigation which seeks to examine the behaviour of dyestuffs in different polymer media, to elucidate the chemical reactions responsible for photofading (3 - 6) and to establish a range of dyestuffs with good lightfastness in the polymers most relevant to conservators (2). These dyed polymers are often not of commercial interest; dyestuff manufacturers do not quote the lightfastness of their products in epoxy resin, for example. This report is concerned with the results of accelerated light ageing of 14 dyestuffs in clear, water-white epoxy, polyester and acrylic casting resins.

2. EXPERIMENTAL

2.1 Resin Casts

Ablebond 342-1 epoxy resin, Metset SW polyester resin and Plastogen G acrylic resin were used. Samples were prepared by casting the resins between Melinex (polyethyleneterephthalate) sheets using 1mm thick microscope slides as spacers. The dyestuffs were incorporated at a concentration of 0.05%. For the epoxy resin, the dyes were dissolved in the hardener component prior to mixing. For the polyester resin, it was necessary to pre-dissolve some dyes in the minimum amount of ethanol (dyes 5 and 6) or acetone (dye 8) prior to addition to the resin. For the acrylic resin, pre-dissolving certain dyes in ethanol (dyes 5 and 6) or acetone (dyes 7, 8 and 13) was also necessary. All casts were cured at room temperature.

2.2 Light Ageing

Samples were aged in uncooled glass cells in the Microscal apparatus with a Philips 400W MB/U lamp. Colour measurements were made initially (t=0), and when ISO Blue Wool Standards 4, 6 and 7 showed perceptible fading (after 11.5, 50.5 and 330h respectively).

2.3 Colour Measurement

Reflectance spectra were recorded from 380 to 710 nm with a Perkin-Elmer 550S UV/visible spectrophotometer with a Perkin-Elmer integrating sphere attachment. The CIELAB values were calculated with a customised software package for an Apple II computer, using data from (7). Results were calculated in terms of CIE source C which represents daylight with a colour temperature of 6500 K. For measurement, the transparent samples were placed normal to the beam (i.e. with direct reflection included) over a standard white background. The samples before ageing had, typically, 70-80% peak transmittance. The reference samples were of standard magnesium oxide. The error in colour difference was estimated as ± 0.7.

2.4 Brief Description of CIE Colour Specification

A simplified description of CIE colour specification has been given by Duff and Sinclair (8); more rigorous treatments are given in various texts (7). The main point is that any colour viewed under given lighting conditions can be specified by three numbers which are derived from the reflectance of the sample over the visible spectrum i.e. that range of wavelengths which the eye can see. These three numbers can be used to specify a point in colour space. Various colour spaces have been described (7), which are useful for different purposes. It is easier to plot two of the three numbers which specify a colour. (Some colour spaces are defined in such a way that the third number can be calculated from the other two).

In CIE 1976 (L*a*b*) space, usually known as CIELAB space, colours are specified graphically, as shown in Figures 1 - 3, by plotting a* horizontally and b* vertically and assuming that L* (the lightness) does not vary greatly. If the samples are all of the same type, as here, this is a valid way of representing their colours. The origin of this plot (i.e. the point with co-ordinates (0,0)) represents white for light-coloured samples, or grey for dark ones, and the primary colours each have their section of the diagram. Colour differences are given by the geometric distance between two points and are shown as a straight line.

3. RESULTS AND DISCUSSION

Table 1 gives details of the colour changes of the clear and dyed epoxy, polyester and acrylic resins at stages corresponding to just perceptible fading of ISO Blue Wool Standards 4, 6 and 7. The CIELAB colour differences of the full range of eight ISO Blue Wool Standards at these stages are given in Table 2.

Figures 1 - 3 illustrate the colour changes of the samples in terms of plots in CIELAB space as described in Section 2.4. These Figures give a clearer visual impression of the significance of the colour changes represented by the values in Table 1. Since the magnitude of the colour changes is given by the distance between points, it can be seen that for the clear resins (numbered 1 in each Figure) ageing results in a change from the white to the yellow section of the diagram. The most severe yellowing is shown by Plastogen G acrylic casing resin. (The total colour changes for the acrylic, polyester and epoxy resins are 27.8, 11.2 and 14.3 (Table 1)). This observation is important since the yellowing of the acrylic medium is likely to be an important component of the colour changes for the dyed acrylic specimens. The final stage of colour change in Figure 1 is therefore plotted with a dotted line to denote uncertainty in the proportion of the overall colour change due to the yellowing of the resin compared to the fading of the dye.

Table 1 Colour changes caused by accelerated light ageing (Microscal, MB/U lamp) of dyestuffs in acrylic, polyester and epoxy media.

DYESTUFF	COLOUR DIFFERENCE (CIELAB)								
	(t=11.5h)			(t=50.5h)			(t=330h)		
	Acrylic	Polyester	Epoxy	Acrylic	Polyester	Epoxy	Acrylic	Polyester	Epoxy
1. Undyed resin	0.6	1.2	0.8	1.8	4.2	2.8	27.8	11.2	14.3
2. Sudan Red BB△	1.4	11.8	14.6*	4.6	39.3	32.2	63.7	71.3	63.2*
3. Sudan Orange R△	2.6	3.4	3.2	2.5	13.2	36.5	19.7	66.5	63.4
4. Sudan Yellow 3G△	0.6	5.0	2.6 1.1	1.5	10.3	5.1 3.3	18.0	37.3	11.9 9.0
5. Zapon Fast Blue HFL△	3.3	4.9 6.2	63.2*	8.2	20.4 17.1	52.8	27.4	33.5 31.8	55.8*
6. Zapon Fast Yellow G△	3.4	15.2	14.3	8.9	29.7	30.8	12.7	38.8	42.9
7. Neozapon Orange RE△	0.5	5.9	4.0	2.0	15.2	14.3	19.0	35.3	31.0
8. Neozapon Orange G△	4.7	8.7	10.7	6.6	14.5	35.6	29.2	21.6	54.7
9. Thermoplast Blue P△	1.5	12.0**	52.8*	2.3	46.8	65.2	49.0	84.6**	96.6*
10. Thermoplast Yellow R△	1.5	5.0	7.9	1.5	5.9	22.5	1.4	10.2	40.7
11. Thermoplast Red B△	1.6	17.7	12.3	1.7	43.6	16.4	2.5	49.1	30.0
12. Orasol Scarlet 2B□	17.5	23.6	11.6	21.2	46.1	11.4	16.7	57.8	13.5
13. Orasol Brilliant Blue GN□	4.5	3.4	54.4*	8.6	8.6	52.8	32.0	19.1	66.5*
14. Cromophtal Blue 4GN DOP□	1.5	1.2	1.0	4.0	3.6	5.4	12.5	15.4	17.2
15. Cromophtal Yellow GR DOP□	1.4	0.6	0.8	0.9	1.4	2.1	5.3	2.2	6.9

* Sample recovered colour when stored in the dark

** Sample continued to change colour when stored in the dark

△ BASF

□ Ciba-Geigy

Table 2 Colour changes in ISO Blue Wool Standards at intervals corresponding to the changes recorded in Table 1

BLUE WOOL STANDARD	COLOUR DIFFERENCE (CIELAB)		
	(t=11.5h)	(t=50.5h)	(t=330h)
1	28.1	48.8	77.1
2	20.5	37.2	70.0
3	13.6	25.1	60.1
4	2.6	5.1	23.7
5	2.1	5.8	23.7
6	3.0	2.0	9.1
7	1.2	0.9	4.0
8	0.9	0.3	1.0

Table 3 Description of Dyestuffs

Dyestuff	C I Generic Name	Chemical Class
2	Solvent Red 24	Di-Azo
3	Solvent Yellow 14	Mono-Azo
4	Solvent Yellow 16	Mono-Azo
5	Solvent Blue 25	Phthalocyanine
6	Solvent Yellow 32	Azomethine (Cr complex)
7	Solvent Orange 54	Cr Complex 1:2
8	Solvent Orange 56	Mono-Azo (Cr complex)
9	Solvent Violet 13	Anthraquinone
10	Solvent Yellow 129	Quinophthalone
11	Solvent Red 139	Anthraquinone
12	Solvent Red 50	Xanthene
13	Solvent Blue 67	Phthalocyanine
14	Pigment Blue 15:3	Beta-Phthalocyanine
15	Pigment Yellow 95	Azo

This uncertainty is much less for the more photo-stable epoxy and polyester resins.

3.1 The Effect of the Resin on Lightfastness

The dependence of the lightfastness on the resin medium can be gauged from the length of the fading curves in Figures 1 - 3 or from the values of colour difference in Table 2. The best comparison can be made from the results after 50.5 hours Microscal exposure; it can be seen clearly that the fading in the epoxy and polyester resins is generally more severe than in the acrylic resin where virtually no fading has occurred at this stage. After 330 hours, the dyed acrylic resin samples still show less colour change but now the yellowing of the acrylic has the effect of exaggerating the dye fading. For practical purposes, however, it is the overall colour change which is important to conservators in the choice of a dye/resin system.

The lightfastness in terms of the eight ISO Blue Wool Standards can be gauged by comparing the colour differences of samples and standards in Tables 1 and 2. Thus, for example, Sudan Orange R,3, and Thermoplast Blue P,9, show overall colour changes of 63.4 and 96.6 respectively in epoxy resin. This is equivalent to lightfastness ratings of 2-3 and 1. Since the high
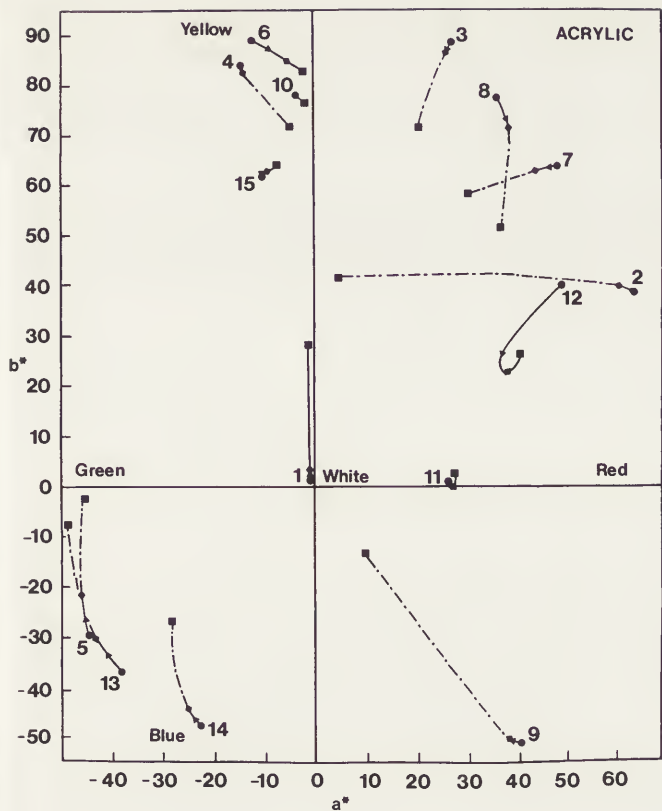
Figure 1   Dyes in Plastogen G acrylic resin.   Change in CIELAB coordinates after 0(●), 11.5(▲), 50.5(♦) and 330(■) hours Microscal (MB/U lamp) exposure.
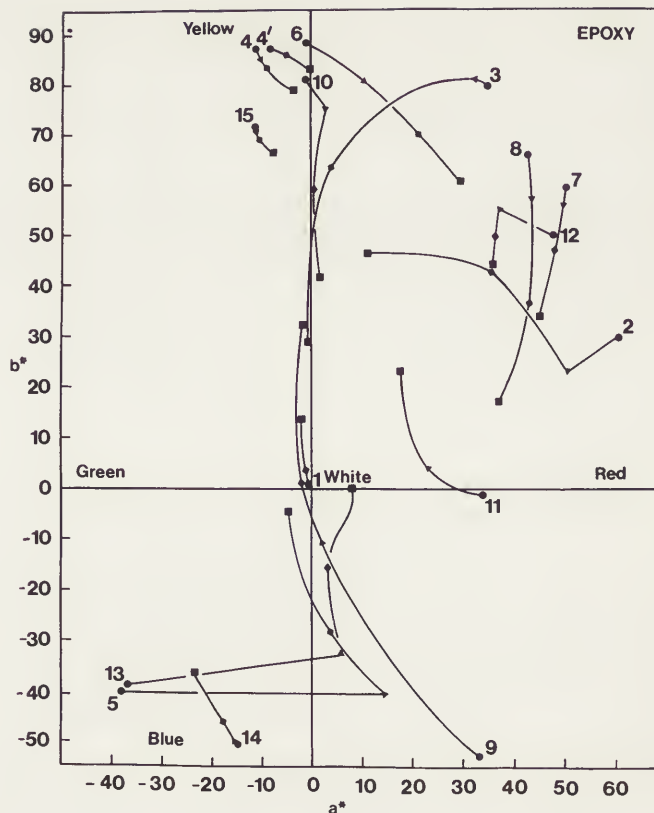

Figure 3   Dyes in Ablebond 342-1 epoxy resin.   Change in CIELAB coordinates after 0 (●), 11.5(▲), 50.5(♦) and 330 (■) hours Microscal (MB/U lamp) exposure.
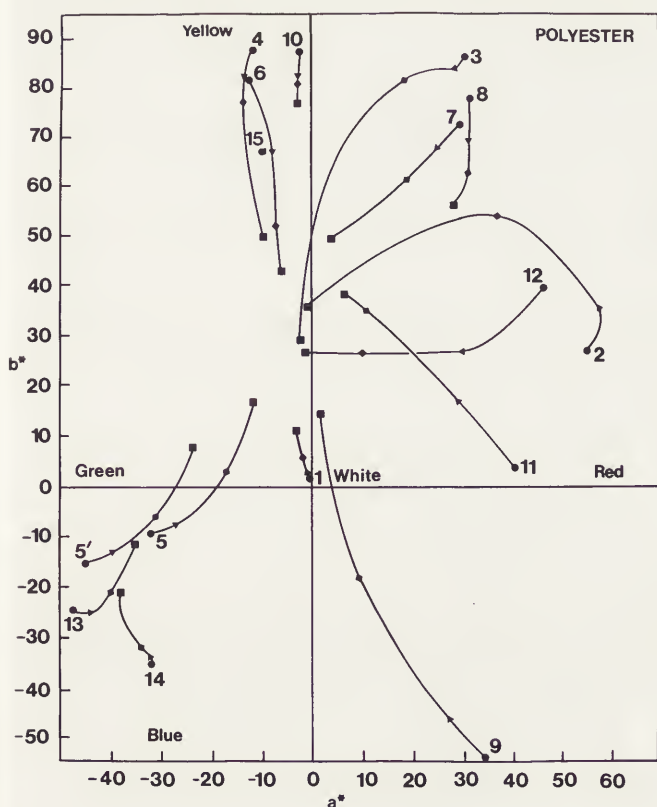

Figure 2   Dyes in Metset SW polyester resin.   Change in CIELAB coordinates after 0(●), 11.5(▲), 50.5(♦) and 330(■) hours Microscal (MB/U lamp) exposure.

pressure mercury-vapour lamp, MB/U, used in this work is best for rapid sorting tests intended to discriminate between dyes of the highest and lowest lightfastness(9) too much emphasis should not be placed on the actual lightfastness ratings.   (The poor spacing of blue standards 4 and 5, Table 2, is an example of the reservations which must be borne in mind with this light source).   A future report will compare the results of different exposure conditions for these sets of samples.

In general, therefore, the acrylic medium is much less detrimental to the lightfastness of the dyes under consideration than the epoxy or polyester resins.   In the case of epoxy resins, studies with anthraquinone and azo dyes (including dyes 3 and 9 from this study) have indicated that the amine hardener is the prime cause of poor light stability (4,5).   For these dye systems mechanisms of photofading have been proposed (3 – 6).

Although most of the colorants examined in this study showed severe photofading in epoxy and polyester resins, samples 10, 14 and 15 displayed good lightfastness in all three resin media.   It should also be stressed that other colorants of good lightfastness in clear epoxy resin have previously been reported (2).

3.2   Anomalous Light Ageing Effects

3.2.1   Stabilisation of the resin against yellowing.

As described above, the last ageing stages of most dyes in Figure 1 show a marked colour change, primarily due to yellowing of the resin substrate.   For samples 10, 11 and 15, however, virtually no change has occurred. The conclusions are that not only do these colorants have excellent lightfastness but they also have the

capacity to stabilise the resin against yellowing. This effect is less readily distinguished for the other resins, but Cromophtal Yellow GR DOP, 15, also stabilises the epoxy and polyester systems. This result is of significance since stabilisation of epoxy resins against yellowing by means of commercial stabilisers has been found to be extremely difficult (10).

3.2.2 Dye-promoted yellowing of the resin.

While some dyestuffs stabilise the resin substrate, other dyes actually accelerate the degradation and yellowing of the resin. This can be demonstrated more clearly by the UV/visible spectra of the dyed resins, as reported previously (11) for Sudan Orange R,3. Another example is Thermoplast Blue P,9, in epoxy resin (Figure 3). In this case the purple dye has faded totally after 50.5 hours Microscal exposure. From that point the fading curve follows the same course as the undyed epoxy resin but the extent of yellowing is more extreme. The changes in both these dyestuffs in epoxy resin have been illustrated in colour elsewhere (11).

3.2.3 Recovery of colour after ageing.

One additional feature of the behaviour of certain dyes during this study is the recovery of colour once light ageing is stopped. This phenomenon was restricted to four dyes, 2,5,13 and, to a lesser extent, 9, and was observed only in epoxy resin. The recovery was in each case greater after 11.5 hours than 330 hours ageing. (The samples were not left to recover after 50.5 hours ageing). The colour changes reported for these samples in Table 1 are the values before dark recovery. The greatest recovery was shown by Zapon Fast Blue HFL, 5. Immediately after 11.5 hours exposure the colour difference was 63.2 but after 315 hours dark storage this value had changed to 47.3. For the same sample, the colour difference after 330 hours ageing was 55.8; this changed to 52.5 after 2 months dark storage. In contrast to recovery of colour in the dark, one sample, Thermoplast Blue P in polyester resin,continued to fade somewhat in the dark after light ageing.

4. CONCLUSIONS

The observations made during this study have many implications for the use of dyed polymers as coatings, or in other ways, by conservators. The importance of testing the lightfastness of dyestuffs in the relevant resin medium is paramount. Also,the yellowing of the resin medium can often dominate the colour changes of dyed samples and one should not generalise about the light stability of polymer classes. Of the clear polymers examined in this study, the acrylic resin yellowed more than the epoxy or polyester resins, in contrast to what would be predicted from the known light stability of many commercial acrylic polymers, such as Paraloid B 72. Anomalous effects such as partial recovery of colour after light fading also serve to demonstrate the complexity of the selection of suitable dyed resin systems for conservation.

SUPPLIERS OF MATERIALS AND EQUIPMENT

Resins

Ablebond 342-1; Conservation Materials Ltd., 340 Freeport Blvd., Sparks, Nevada 89431, USA.
Metset SW; Metallurgical Services Laboratories Ltd., Reliant Works, Brockham, Betchworth, Surrey RH3 7HW,UK.
Plastogen G; Frank W. Joel Ltd., Oldmedow Road, Hardwick Industrial Estate, King's Lynn, Norfolk,PE30 4HH, UK.

Dyes

BASF, Dispersions and Pigments Division, PO Box 4, Earl Road, Cheadle Hume, Cheadle, Cheshire, SK8 6QG, UK. Ciba-Geigy Plastics and Additives Co.,Pigments Division, Roundthorn Industrial Estate, Wythenshawe, Manchester, M23 9ND, UK.

Apparatus

Microscal Light-Fastness Tester; Microscal Ltd., 79 Southern Row, Kensal Rise, London, W10 5AL, UK.

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11. Tennent, N.H., "Polymers in Art Conservation", Shell Polymers 6 (1982) 14-17.

Section 17

Climate and Lighting Control

Contrôle de l'éclairage et de la climatisation

CONTROL OF CLIMATE AND LIGHTING

Coordinator : G. de Guichen (Italy)

Assistant   : B. Ramer (Italy)
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              C. Aranyanak (Thailand)
              J.M. Arnoult (France)
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              S. Weintraub (USA)

Programme 1981 - 1984

Climate

1.   Case study: the influence of climatic
     conditions on a building.
2.   The showcase: mechanical climate control.
3.   The showcase: passive climate control.
4.   Studies on buffer material other than
     Silica gel.
5.   Measurement of air leakage from show-
     cases.
6.   Measurement of relative humidity and
     temperature inside a showcase using
     microprobes.
7.   Developing ways of creating a micro-
     climate in museum buildings and
     religious architectural monuments.

Lighting

1.   The reconciliation of controlled lighting
     conditions with the aesthetic demands of
     art galleries.
2.   Lighting - anti-U.V. films - artificial
     ageing.

EXPERIENCE WITH SILICA GEL FOR CONTROLLING HUMIDITY
IN SHOWCASES

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SUMMARY

Most galleries in the Victoria and Albert Museum,
including the temporary exhibition gallery, are not
air conditioned so it is important to improve the
conditions, locally, within showcases wherever
possible. This report describes the experiments which
were carried out with silica gel in standard and
specially built showcases of a size commonly used in
the V&A, with the showcases standing in rooms where
there was no control of conditions other than heating
in winter.

Experiments with two showcases in the laboratory

Showcase design: Volume 1 cubic metre. Metal framed,
glazed with hinged doors on the narrow ends, wooden
baseboard, no lights inside case, glass top. Silica
gel below baseboard in a wood and polythene
compartment.

Room conditions: No air conditioning, heating only in
winter, temperature variations 14 - 27°C.

The 1 cubic metre volume case is used
extensively in the V&A for all types of objects.

One showcase was used as a control, it was fitted with
the same compartment and baseboard holes as the
showcase containing silica gel but no silica gel was
put into it. Thermohygrographs were used to record
the humidity. This meant that the showcases were
opened once a week for chart changing. There was
very little difference in the readings obtained from
a thermohygrograph suspended in the centre of the case
and one sitting on the baseboard. There was also no
significant change between having small holes (8 cm
diameter) cut between the baseboard and the silica gel
compartment and later work with a large hole
(75 x 35 cm) cut and covered with wire mesh. So it
would seem that diffusion throughout the case and from
case to silica gel compartment was adequate. Tests
continued from 1978-1983 when the cases had to be
moved for building works. The 20 kg of silica gel
(in 1 kg bags from W.R. Grace) was conditioned to
55% RH and replaced with freshly conditioned gel every
6 months. The graph (1) is typical of results
obtained every year. It shows the humidity changes
taken from the thermohygrograph charts using the method
suggested by Organ, mode (average) being found by eye,
using a thread as a guide. The vertical lines join
the maximum and minimum values for each week. The mode
points are joined up for convenience, the slope of the
line does not indicate the rate of change of humidity.

In 1979 it was decided to see what the effect on the
showcase would be of adding an "object" and what the
effect of the silica gel on the object would be.
Pieces of pine timber of a convenient size to be
handled and weighed were used, the same weight
(13.5 kg) in each showcase. The size of the object in
relation to that of the showcase was similar to that
where several small objects are shown in one showcase.
The special situation of a large piece of furniture in
a showcase only slightly larger than the object has

not yet been studied. The variations in humidity in
the showcase continued to be similar to those shown by
the empty cases during the previous year. The graph
in Figure (2) shows the change in weight of this
"object" in the two showcases with and without silica
gel. The results are not easy to interpret, they do
not follow the humidity variations which are very
similar for both showcases and also similar from year
to year. There is no sudden change in conditions in
the cases to explain the greater increase in the
weight of the wood in the silica gel showcase that
occurs in 1982.

It appears that the silica gel reduces the short term
variations in humidity when compared with the much
larger variations in the room but does not remove the
longer term seasonal variations. This accords with
other experience, e.g: Ramer Studies in Conservation
1983. The silica gel does not hold the humidity at
55% RH. To avoid confusion the results for the
showcase are not included in Figure (1) but are very
close to those for the silica gel case with the same
result; short term fluctuations are reduced,
long term ones are not. A disappointing result.

The buffering effect of a showcase alone, without
silica gel, is found in the V&A Jewellery Gallery with
a 3 cubic metre volume case made of metal and glass
with sliding doors at the front and fluorescent tubes
in a sealed compartment above the case, Figure (3).
The showcase, which contained no silica gel but had a
blockboard back, baseboard and shelves adding to the
buffering effect, reduced the short term fluctuations
in comparison with the large variations in this room,
ventilated and temperature-controlled but with no
humidification. The humidity does not stay steady,
nor in the mid fifties which would be best for the
objects.

Experience in temporary exhibitions

The temporary exhibition gallery 45 is heated in winter
with warm air through ducts and has a little, but
inadequate, humidification. The temperature varies
considerably, 14 - 27°C in a year, similar to the
laboratory, and most of the galleries in the Museum,
and the humidity fluctuates greatly as can be seen in
figures 4 and 5. Two types of showcase were studied.
First 0.1 and 0.25 m³ cases made for panel paintings
from blockboard with glass fronts and with silica gel
in a wooden compartment in the base or sides covered
with a removable panel for changing the silica gel and
lined with polythene. Air movement between the silica
gel and object compartment was through a full length
gap 2.5 cm wide. There were no lights in these
showcases, they were lit by spotlights from some
distance away, Figure (4). Second 1.5 and 3 m³ metal
framed and glazed cases with sliding doors on the long
side, made especially to be silica gel conditioned
and as air tight as possible (designer Paul
Williams). The lighting was by low voltage spotlights
in a compartment on top of the showcase. There was
a wooden compartment below the baseboard which had
many 2.5 cm diameter holes cut into it, covered with
decorative cloth, to hold the silica gel. Some cases
had a side opening to remove trays of loose silica
gel, others had a hinged flap in the base. Silica gel
bags were also hung under the sloping case furniture
but these were not accessible to be changed during
the exhibition. There was no space for thermo-
hygrographs in either of these types of case and so
dial hygrometers were used and read every weekday.
These were fixed to the wooden case furniture which
would have had a local buffering effect, this may
explain the small variation in humidity but this may
be due to the effectiveness of the silica gel.
The objects, paintings and miniatures, were also fixed
closely to the wood, so the measurements would relate
to the conditions that the objects were subject to.

Again it is observed that the short term fluctuations
in humidity were reduced in comparison with the wider
variations in the gallery but the showcase humidity
followed the longer term trends and did not stay steady
nor did it stay at 55% RH. Silica gel conditioned to
70% RH was used in an attempt to push the humidity up

to a more acceptable level, this did not work. Results were similar for panel painting cases in three temporary exhibitions; Princely Magnificence 15 October 1980 - 1 February 1981, Splendours of the Gonzaga 5 November 1981 - 31 January 1982 and Artists of the Tudor Court 9 July 1983 - 6 November 1983. Before the Artists of the Tudor Court exhibition experiments were carried out in an empty panel paintings case, using first silica gel at 55% RH and then at 70%. The silica gel lost a lot of weight and at one point the humidity did reach 60% but mostly it stayed at 40%, similar to the humidity in the room. It must be concluded that the moisture, many times more than needed to raise the humidity from 30 - 55% RH was lost through leakage or through the timber, or absorbed into it. Replacing the silica gel three times to thoroughly condition the case itself did not improve the results, so presumably the water was leaking away. Similarly with the larger metal framed cases, the silica gel lost weight, humidity went up from 31% in the room to 44% in the case but no higher. When the case was opened the humidity dropped and when it was closed rose again to 43%, so the silica gel seemed to be having some effect but not enough.

Conditioning of silica gel

This was done first in an environmental test chamber (climate chamber) made by Votsch. This was not designed for this job and conditioning a large number of silica gel bags packed tightly together took 3 - 4 months. Smaller batches were quicker but for use in a big temporary exhibition, let alone permanent displays, large amounts are needed and several small batches added up to the same time as a large amount done in one batch. Later a small room was found to be used for conditioning, this is in a semi-basement area with stairs and no lift. Movement of 50 kg drums between conditioning room and the temporary exhibition gallery was extremely laborious. The room was fitted with a commercial humidifier/dehumidifier unit, which is effective but the silica gel needs to be spread thinly if loose, or if in bags these must be hung separately on poles. If they are laid on shelves or bunched together they do not get properly conditioned.

Other problems

Sealed metal and glass cases are expensive, it is cheaper and easier to make them from wood, chipboard and blockboard. It is nearly impossible to make an openable showcase which is airtight and there is the same problem with the silica gel compartment, which should be openable to change silica gel during the exhibition, if necessary, but not leak. Drawers have been tried but leak or stick, screw flaps take too long to open and loosen with repeated use, but seem to be best especially if the opening is small and trays of silica gel are pushed in one after another, with strings attached to get them out again. The silica gel adds from 10% to 25% to the weight of the case, a problem when fixed to walls or on temporary flooring. When an exhibition is being set up cases are open most of the time as each object, and its label, are positioned to everyone's satisfaction. This is bad for objects and silica gel, so the room needs to be humidified at this time, also to precondition the timber in cases which is usually very dry. The V&A temporary exhibition gallery is too big and open to humidify, the ducted air is not adequately humidified and humidifiers have only a very local effect which is lost about 2 metres away from the source.

Designers and curators do not like to see thermo-hygrographs, or even dial hygrometers, in cases or galleries. A small, reliable humidity probe is not yet available for use in these circumstances but we hope to be able to do some remote monitoring soon.

Conclusions

It seems from these poor results that silica gel is really not worth the trouble, time and expense in purchasing, preparing and handling it and in designing and building showcases to accommodate it. The effort necessary for temporary exhibitions appears to be out of proportion to the results obtained. The ordinary showcase without silica gel is nearly as good (or bad) in reducing short term fluctuations. A totally metal and glass or plastic case, well sealed, is essential (Ramer Studies in Conservation, 1983). This would be very costly on the scale needed at the V&A where a massive investment in showcases already exists. Wooden case furniture is a useful additional buffer but in a sealed case is a risk for metal and other objects which can be damaged by wood acids.
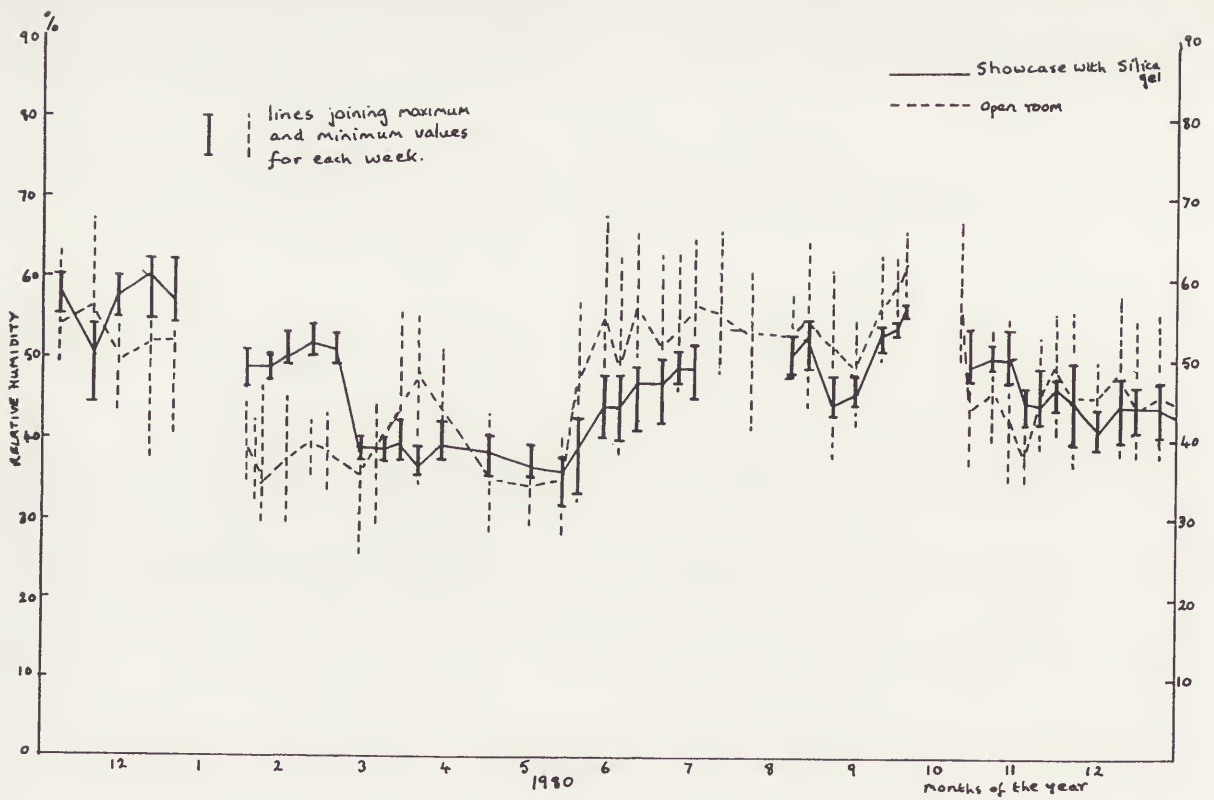
Figure 1.   Experimental case with silica gel in laboratory 1978–1983
This year is typical of all 5 years

Figure 2.   Weight loss of wood "object" in experimental showcases in laboratory
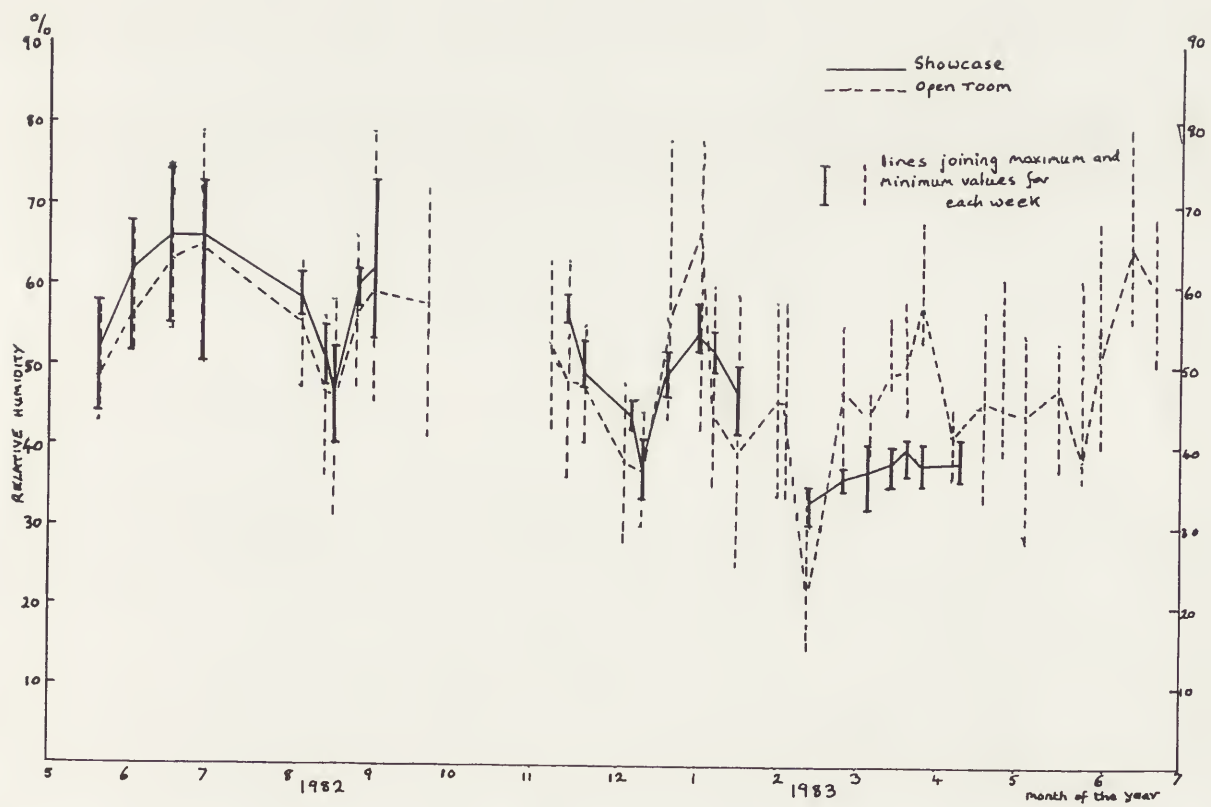with and without silica gel.

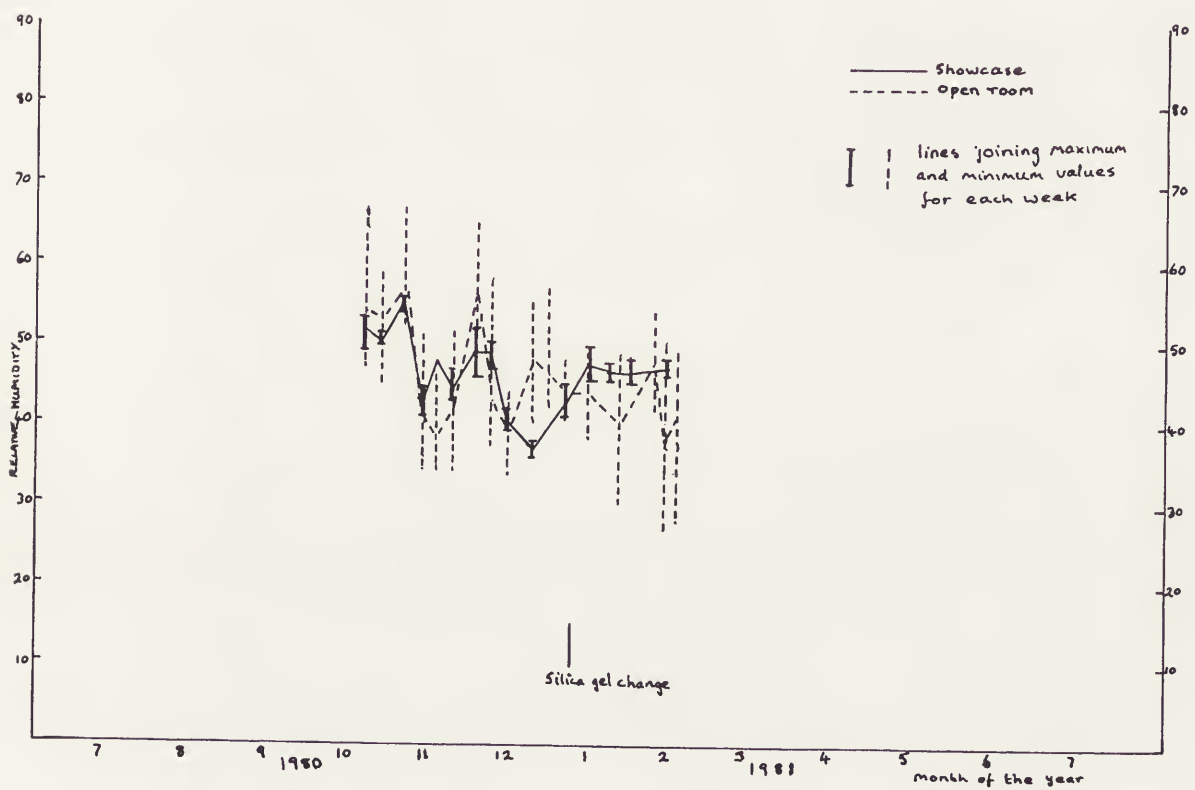Figure 3. Humidity variations in Jewellery Gallery, showcase with no silica gel.

Figure 4. Panel painting showcase with silica gel in temporary exhibition gallery 45.
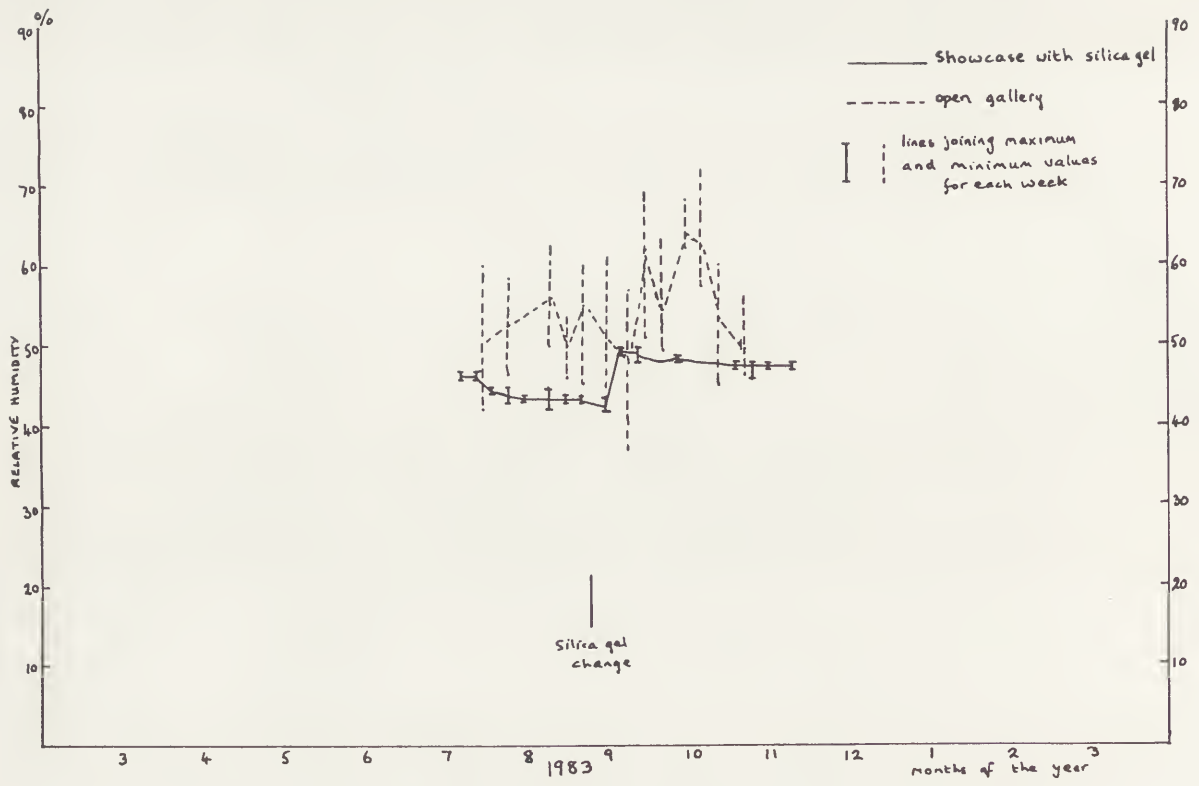Princely Magnificence 15.10.80 - 1.2.81

Figure 5. Metal and glass miniatures case with silica gel in temporary
exhibition gallery 45. Artists of the Tudor Court 9.7.83 – 6.11.83

CLIMATE CONTROL: THE EGYPTIAN GALLERIES AT THE
METROPOLITAN MUSEUM OF ART

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SUMMARY

The purpose of this paper is to describe the three
different approaches to climate control that were
attempted in the recently completed Egyptian galleries
of the Metropolitan Museum. I will also try to shed
some light on some of the reasons for the gradual
evolution away from air-conditioned cases toward the
use of sealed cases within air-conditioned gallery
spaces. Finally I will describe the procedure used
for testing these sealed cases.

Phase I

In June 1983 the Department of Egyptian Art at the
Metropolitan Museum opened the third and final series
of galleries concluding a project begun in 1972 to
reinstall the Egyptian collection in its entirety.
All estimated 40,000 objects are now on view in thirty-
two climate-controlled galleries, occupying nearly one
and two-thirds acres of exhibition space.

Of the many problems facing the curatorial, conserva-
tion, architectural and engineering personnel in
undertaking a project of this scale few were more
formidable than the problem of climate control and
case design.

The first series of eleven galleries opened in 1976.
In planning for this first phase of the installation
the Curator (Dr. Christine Lilyquist) made the deci-
sion to attempt to display all objects -- following
a general recommendation by the architect Kevin Roche
of Kevin Roche, John Dinkeloo and Associates -- and
to simultaneously place them in chronological order.
The ramifications of this decision meant displaying
objects with different environmental requirements
together (i.e. ivory, bronze, linen and stone) in
the same case. It also meant that very large cases
would be required to accommodate objects of greatly
varying scale and allow ease of access to them.

The resulting design scheme called for large (450 -
9500 cubic feet) walk-in cases fronted by 7½ x 7½ foot
tempered glass lights butted one against the other
with a small air space between each panel. In order
to make this kind of large display case satisfactory
from a conservation standpoint the consulting engi-
neers(John J. Altieri, P.E. Consulting Engineers)
designed a separate air-conditioning system for the
cases themselves. The concept was to provide a close-
ly controlled (72° + 1F -50 + 5% RH) temperature and
humidity treated supply of super-clean air to the
cases. This air was to exfiltrate through the joints
between the glass panels into the public areas due to
higher vapor pressure in the cases. The public areas
were air-conditioned to comfort conditions by an
existing system, and return air from this system was
the source of supply air for the case air-conditioning.

Low voltage incandescent lighting fixtures were mount-
ed in compartments inside the ceiling of the majority
of the cases, providing 75 watts per lineal foot of
casework. This lighting, together with the trans-
mission load from the surrounding spaces, constituted

case cooling load.

Large load savings occurred when the lighting was
turned off at night. Separate zoning was required for
virtually each case, with sensors within the cases to
vary the incoming air temperature and compensate for
the case loads.

The volume of air required to maintain pressurization
and proper temperatures and humidities resulted in
approximately 15 to 30 air exchanges per hour.

Filters were provided in the inlet and outlet to each
zone. These filters were 99.97% HEPA filters normally
used in controlling radioactive exhausts, screening out
particulates to .3 of a micron in size. The effective-
ness of these filters was somewhat compromised in sev-
eral cases where the new case-supply ductwork was con-
nected to existing riser ducts which were old and dirty.
The result was that loose duct lining and particulate
matter could enter the air stream after filtration
occurred, creating a maintenance and potential conser-
vation problem in these cases.

A system of continuously operating 35.6 ton capacity
dual reciprocating compressor machines provided 40° F
chilled water to coils located in each zone. A pneu-
matic control system maintained a saturated discharge
temperature off the cooling coils in summer to maintain
fixed humidity, with reheat coils maintaining tempera-
ture. In winter, humidity was provided by steam grid
humidifiers with humidistats controlling steam flow.

These steam grid humidifiers turned out to be the most
troublesome feature of this system. On numerous occa-
sions a humidifier would stick in the full-open posi-
tion and quickly fill the case with live steam, result-
ing in condensation on the objects and interior sur-
faces of the casework. Some damage to objects resulted
from these incidents and the conservation and curato-
rialstaffs soon found themselves in the uncomfortable
position of having to protect the art from the system
installed to protect it in the first place.

It was at this time that I and another member of the
Egyptian Department conservation staff began to monitor
conditions inside all of the cases using recording
hygrothermographs. This process was invaluable in
determining the seriousness of system malfunctions,
and provided a useful diagnostic tool which the engi-
neers could eventually use in prescribing remedial work
and in planning the design of the systems that were to
follow. We now have some thirty-six hygrothermographs
in place throughout the wing, and while it presents a
considerable maintenance chore it remains the most
reliable way the Egyptian Department staff can know
with any certainty that conditions inside the cases
are not presenting a danger to the objects.

After about two years of operation it became obvious
that substantial remedial work would be necessary to
correct the shortcomings of this system. A number of
modifications were made to provide for more stable
operation and for better notification in the case of
mechanical failures. These devices included a backup
shutoff solenoid valve in the feed of the steam humidi-
fiers controlled by high limit humidistats located in
each case. In the event of the RH level exceeding 60%
inside a case the solenoid valve then shut off the
steam supply for the entire case system and sounded an
alarm in the engineers office. Other modifications
made at this time were the addition of a backup chiller,
backup pumps and a booster fan to improve air distribu-
tion in some of the cases and the addition of insula-
tion to the backs of casework that were located against
exterior walls. In general, these measures were effec-
tive; however, this system will always require careful
monitoring and maintenance to assure its stable opera-
tion,

Phase II

Phase II consists of nine galleries opened in November
1978. It presented an opportunity to improve the cli-
mate control design of Phase I. This design provides
for dual chilling equipment with a complete system of
electric-electronic controls. Fogging devices (cold

water particles broken up by compressed air sprayed into the cooling coil) maintain a fixed dew point on all air supplied to cases. The case system and surrounding gallery system are conditioned to a space dew point of 50% RH. For each system a dew point master controller (hygrometer) raises or lowers dew point to match space conditions as sensed.

Should the gallery become heavily occupied, the rise in moisture is sensed as an increasing dew point. The dew point control acts to modulate the chilled water valve open, lowering supply air temperature (dehumidification). The various case and zone reheat coils modulate to maintain temperature.

Should there be a reverse -- a fall in sensed dew point -- the dew point control acts to modulate the chilled water valve closed. In this manner, little or no dehumidification occurs, and warmer moisture-carrying air is supplied.

Reheat is provided using SCR (silicon controlled rectifier) controlled electric heaters. The SCR provides closely controllable, constantly variable power to the heaters.

The Phase II system achieved a much more stable operation in comparison to Phase I. System problems were reduced due to a number of factors, including single control of moisture content inside all of the cases; electronic rather than pneumatic controls; electric rather than water reheat; less dust in cases because system used no outside air; better distribution of air to cases and, most significantly, in the event of mechanical failure, the foggers did not fill the cases with humidity.

In spite of the obvious improvement of this rather elegant system over its predecessor, the first 18 months of operation were plagued by a host of mechanical and control problems. Some of these problems included impurities in the water supply to foggers which caused them to clog frequently and resulted in unacceptable RH fluctuations; difficulty in servicing the SCR's and some of the other sophisticated electronic control devices; difficulty in maintaining temperatures during peak load periods due to lack of adequate chilled water capacity; presence of dust in cases due to ongoing construction in the area. These problems were eventually resolved, and the system is now capable of providing $72^\circ F$ - 50% RH conditions in a reasonably stable manner.

However when it came time to make a decision regarding the design of Phase III system, the Phase II system was not operating satisfactorily. This fact, in conjunction with the ongoing problems of the Phase I system, helped to create an atmosphere in which the Egyptian, Objects Conservation and Textile Conservation Departments found it impossible to support another attempt at air-conditioned cases.

By this time the museum staff had had enough experience with the various problems associated with Egyptian Wing air-conditioning to make the following basic assumptions about the long-term effects of air-conditioned casework.

1. Even under the best of circumstances, no air-conditioning system would be capable of providing constant temperature and relative humidity day in and day out, 365 days a year. Mechanical failures were inevitable, and deviations from mean temperature and RH -- lasting anywhere from a few minutes to a few days -- could be expected.

2. The Textile Conservation Department expressed the concern that air constantly pumped into the cases was creating an oxygen-rich environment which could increase the rate of oxidation for the organic materials being housed therein. Also, the presence of particulate matter in the cases along with staining of the wall linen at air outlets suggested the possibility of pollutants being introduced with the air, steam, or both.

3. The increasing complexity of the systems and controls being installed required more maintenance, and in some cases more expertise, than the museum's Buildings Department could provide at that time. Even now the manpower needed just to keep the various controls, sensors and alarm devices in proper calibration exceeds what the museum's staff can provide, with the result that outside contractors are hired to supplement their efforts.

It was against this background that the decision to eliminate air-conditioning from the Phase III cases was made.

Phase III

It was decided that temperature and relative humidity in the entire gallery space would be controlled by an upgraded HVAC (heating, ventilating and air-conditioning) system. To implement this, two new cooling towers were installed not only to run Phase III but also to add supplementary cooling capacity for Phases I and II. In addition, new chillers, pumps, two new fans, and an enthalpy control system with an economizer cycle were installed.

In spite of these and other improvements, it was anticipated that there would be some daily variation in RH and occasional mechanical failures. The casework was therefore designed to be sealed so that the RH in the cases would remain stable in the event of short-term fluctuations in the gallery space. It was felt that in order to be effective, the cases should at least be able to slow down air exchange over a period of several days in order to maintain a stable RH environment during periods when the system was "down". This would also make it possible for the cases to be retro-fitted with silica gel as an RH buffer should a special environment be required.

The success of this approach hinged solely on whether or not sealed cases of the size required (up to 2100 cubic feet) could be constructed to meet the conservation staff criterion of one and one-half air exchanges per day. The idea of sealed cases had been brought up by the conservation staff previously, mainly in discussions concerning the climate-control design of Phase II. The concept was ultimately rejected as being impractical, if not impossible, if curatorial access to the cases was to be a factor. This time however it was decided to assess the feasibility of sealed casework by having the architect design a full-scale prototype case which would be rigorously tested by conservation staff prior to making final design decisions regarding Phase III.

A prototype case was constructed in which all of the moveable elements were carefully sealed. Access to the case consisted of pivot and sliding doors which, when closed, were sealed top and bottom by a moveable neoprene gasket which was ratcheted into place. The problem of dissipating heat load from the lighting fixtures was solved by locating fixtures in a special chamber above the case and directing return air through these chambers, thereby removing the heat. To accurately determine whether the cases met the design specifications a method was developed by Steve Weintraub of the museum's Objects Conservation Department to test them.

Test Procedure

Briefly described, the testing procedure consisted of filling the cases with carbon dioxide or helium (CO_2, because of its weight, worked better for testing the lower parts of the case and conversely, helium worked best for testing the leakage along ceiling joints) and then measuring the rate of the tracer-gas loss by a "Gow-Mac" gas analyzer fitted with a strip chart recorder. Further, in order to test the integrity of the seals and to detect specific points of leakage, a gas leak detector with a probe attachment was used, making it possible to improve seal integrity where needed until the case would conform with design criteria.

On the basis of this prototype and this testing method, it was possible to avoid costly or irreparable mistakes during the final design construction and installation stages of Phase III. The contractor who installed the cases worked closely with conservation staff and was able to modify and improve seals in response to test results. This resulted in even the largest of the

finished cases being acceptable in their ability to
maintain RH stability over a considerable period of
time.

Conclusion

Based on a year's observation of the Phase III system
it is possible to state that air of constant tempera-
ture and humidity surrounding well sealed and buffer-
ed cases does indeed result in very stable relative
humidities inside the cases, even during periods of
instability in the gallery system. The mass of the
casework and the hygroscopic material within them
help to maintain this stability even with fairly wide
fluctuations in gallery temperature and relative humi-
dity.

It can be noted at the same time that with "in-case
air-conditioning" systems, such as Phase I and II,
operating costs can be reduced when loading and oper-
ating of central air-conditioning systems are reduced
(i.e. in case of an emergency or for economic consi-
derations, the case system can be run independently
of the gallery system with great savings in energy).
However, the greater stability afforded by using
tightly sealed cases in conjunction with continuously
operated central air-conditioning, and the increased
safety of the objects displayed in this manner, lead
me to strongly recommend this alternative.

Acknowledgements

AN EASTER ISLAND EFFIGY FIGURE DISPLAY CASE

Richard O. Byrne

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In 1843 the whaler Margaret Rate, Captain
Coffin, hove to off the shore of Easter
Island to replenish supplies. Captain Coffin
declined to allow the crew to land, judging
the inhabinets untrustworthy after the ship
was pelted with rocks. However, trading did
occur by canoe. In addition to foodstuffs
some ethnographic artifacts were obtained
including a zoomorphic image representing
either a seal goddess, or a bird used in the
annual bird king ceremonies. On the return
of the Margaret Rate to Saint John, New
Brunswick (N.B.) the effigy was donated to
the Mechanics Institute which in turn became
the New Brunswick Museum. Thus, by canoe and
whaling ship a very important and probably
unique Easter Island artifact entered a
Canadian collection.

Over the years the effigy figure became
extremely desiccated. Made of reeds and
covered with tapa cloth, the effigy figure
was in a very friable and fragile condition
that made it almost impossible to handle the
object without some loss of grass and tapa
fibers when it arrived at the Moncton, N.B.
Canadian Conservation Institute's regional
laboratory in 1975.

John Grant of the CCI staff was assigned the
task of its conservation. Following his
close examination, which included the taking
of X-rays, he concluded that the bird could
be stabilized with a combination of a thick
methyl cellulose paste to tack down loose
fibers followed by a general application of
a 5% PVA/AYAF impregnation. The object was
also "dry" cleaned with methyl alcohol to
remove surface grime.

It was also decided to construct a special
case made of plexiglass with wooden end
supports. The effigy figure would be then
placed in the case and the case charged with
nitrogen gas. This would reduce future harm
to the object by excluding oxygen and
moisture, and also reduce risk to the object
from idle handling.

Richard O. Byrne was assigned the task of
constructing the case and mounting the figure.

A 20 cm diameter by 76 cm in length clear
plexiglass tube was selected with walls 6.3
mm thick as the case. The ends of the tube
were machined as flat as possible in order
to receive end caps made from flat 6.3 mm
plexiglass discs.

On the inside at one end was mounted an
aneroid barometer which had a new scale
affixed to it which would indicate when the
pressure in the case dropped below the
highest recorded level of barometric
pressure recorded in Saint John, N.B. in the

past 50 years. Though the barometer is in an
enclosed tube and hence subject to pressure
change due to temperature changes, it is
considered a reasonably accurate indicator of
what is going on inside of the tube. Namely
what one really wants to know is, is there
still a firm charge of nitrogen gas present?
The barometer was an inexpensive instrument
that would tell this.

At the other end of the tube a gas valve was
installed in order that the tube could be
charged with pure nitrogen gas. The tube was
carefully drilled and threaded to receive a
series of screws to lock the caps firmly in
place. The end caps were then sealed in
place using silicone rubber to form a gasket.

A curved plexiglass mount that followed the
curvature of the effigy bird was constructed
with a clear plexiglass band affixed. The
band applied a very slight positive pressure
on the effigy figure to help hold it in place.
Then with the effigy figure cleaned and
conserved it was mounted and slid carefully
into the tube. The tube was sealed and
charged with gas. Leaks were allowed to
continue until it was certain the tube was
flooded with nitrogen and purged of oxygen.
Though not a "scientific" approach that
ensured the removal of oxygen, it was
inexpensive to waste a quanity of nitrogen
gas rather than get involved in the expense
of costly gas monitoring equipment. The
internal barometer was used as the indicator
as to when leaks had been sealed by the
careful application of pressure to the end
caps by selectively tightening the retaining
screws. Once free of leaks the barometer
registered well above the selected high
barometric level chosen as a baseline.

Once sealed in its tube the effigy figure was
transported by car from Moncton, N.B. to
Saint John, N.B. and placed back into the
museum's storage.

Eight years later we can look back and see
how well this special display case has
performed as a micro climate and protective
barrier against harm. What has happened?

First of all after four years it was noticed
that the case was loosing pressure. Since
the museum did not have a supply of nitrogen
gas, the effigy figure had to be taken to a
commercial gas supplier to be recharged.
This undesireable handling and travel could
be avoided if the museum were to purchase a
small laboratory bottle of nitrogen gas.

One should note here that removing the sealed
case from a rather stable museum environment
into a car for transport not only will cause
a rapid temperature change in the tube, but
also the mount is designed for stable display,
not the random bumping of a car ride. If the
effigy figure is to be transported, a separate
transport case should be provided for it.
Also, the handling and recharging of the case
implies that a staff member should receive
special instructions in the object's care.
Future care should be spelled out in a
"operator's manual" for the case.

Second, it would be prudent if other cases
are built like this to provide for a second
gas valve on the opposite end to ensure
venting of the oxygen. This was a design
flaw in our model.

Third, the case has been opened and the mount
modified so that the plexiglass holding band
has been replaced with a shear stable fabric
(Stabiltex-Swiss Silk Bolting Co., Zurich,

Switzerland). The effigy figure can now be better seen.

Fourth, the case has proven its worth by protecting this extremely rare object from serious damage when the storage area was fumigated with an oil based pyrethrim by a commercial fumigator. Inadventantly the misting equipment was set up close to the effigy figure and a sizeable quanity of oily fumigant collected on the plexiglass. Had the effigy figure been unprotected it would have been greatly damaged. As it is the plexiglass is seriously damaged and clouded over. The two end support boxes are less than charming.

Fifth, it is our opinion now that a humidity indicator strip should be included in the case, and future recharging with nitrogen should be done by first bubbling the gas through a water bath.

In conclusion, one can say that the forsight of suggesting this special case as part of the objects conservation has saved one of the rarest and most fragile items of Easter Island. One can also conclude, that the conservation of an object, regardless of how special its display case and environment, is an ongoing process that requires constant observation, monitoring and fine adjustment.

(I wish to thank John Grant of CCI for his help in the preparation of this paper).

Fig. 2   End view of the display case showing the modified dial on the aneroid barometer.

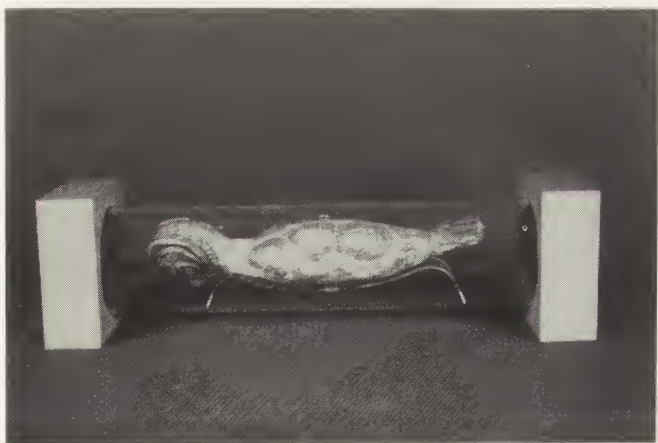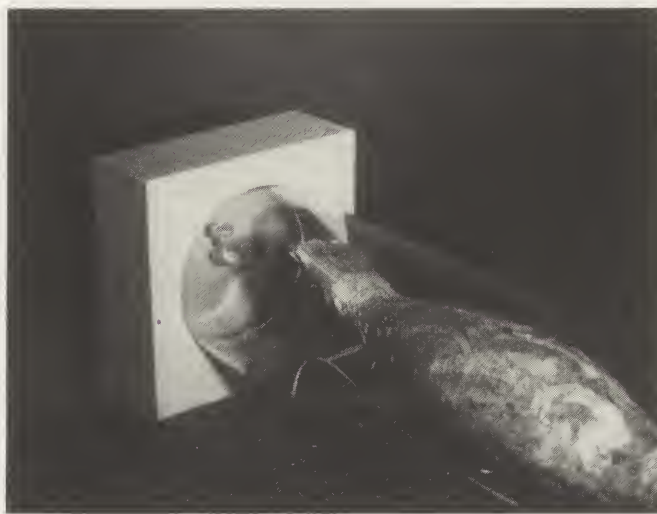Fig. 3   Gas valve shown on the other end of the display case.

Fig. 1   An overall view of the display case and the mounted effigy figure. The case was initially charged with nitrogen gas to 109.5 kpa. Normal atmospheric pressure at Saint John, New Brunswick never exceeds 103.1 kpa. The case is recharged with nitrogen gas from time to time to maintain the 109.5 kpa level.

PROPOSAL FOR A TYPOLOGY OF DISPLAY CASE CONSTRUCTION DESIGNS AND MUSEUM CLIMATE CONTROL SYSTEMS

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SUMMARY

Drawing on published reports of experiments in Museum Climatology, an attempt has been made to propose a standardisation of terminology by grouping and classifying the more commonly used types of case construction designs. The formulation of a typology for different museum climate systems was also developed simultaneously. Case studies in which different methods have been used to create microclimates within museum cases, are used to illustrate the usefulness of such a typology. It is intended to tighten up language and interpretation in a field characterised by the use of either imprecise terms, such as 'ventilated', 'sealed', 'hermetically sealed' and 'airtight' to describe qualitatively the "sealedness" of a case, or complex mathematical formulae to quantify the "leakiness" of a case in terms of microclimate control.

1. INTRODUCTION

Before a detailed discussion of the proposed typology is undertaken, a brief reference to the parameters within which it has been tabulated, should first be considered.

This diagrammatic scheme has been devised taking into consideration only, the control of Relative Humidity. Since the microclimate control of museum display cases is essentially a simple system of protection against the adverse effects of fluctuations in humidity and temperature, the control of entry of both gaseous as well as particulate forms of pollution and dust, are considered as secondary to, and only as a consequence of, the control of humidity and temperature in museum display cases.

By discussing construction methods which reduce leakage of air to a minimum, the typology places emphasis on "impermeable" construction materials to promote RH control, in particular for organic materials. For certain metals, on the other hand, an adequate ventilation rate, rather than minimal air exchange, may be more desirable to dissipate harmful vapours.

Therefore, in using this typology of museum case construction design and climate control systems, it should be remembered that it focuses on the requirements for stabilising Relative Humidity variations, and that a distinction should always be made between the priorities for the display of organic materials and those for metals.

2. BASIC DISPLAY CASE CONSTRUCTION DESIGNS

The following four basic types of display cases in current use in museums, have been extrapolated from publications:

SYMBOL 2.1.   DESCRIPTION

TYPE: Case in which there is free air exchange between the inside of the case and ambient gallery conditions.
EXAMPLE: Commercially available standard stock in which no attempt has been made to lessen air exchange.
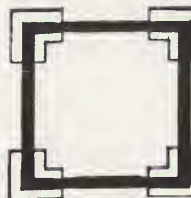
DESCRIPTION OF MATERIALS: The frame is made of either metal or wood. In older cases, wood is the more likely material. This may be painted or unpainted. The panes are more commonly made of glass, and would be in either doors on hinges with an ordinary lock for security, or in sliding-door type with a gap between the panes. Most museum display cases fall within this category.

FUNCTION: ADVANTAGE: protects against theft and vandalism.
DISADVANTAGES: does not modify adverse ambient environmental conditions. The climate inside the case will reflect, with a minimum time-lag, depending on the buffering capacity of the materials of the case itself, the climate surrounding it. It allows the free passage not only of air, but also of dust, dirt and pollutants.

SYMBOL 2.2.   DESCRIPTION

TYPE: Cases in which a reduction of the exchange of air between the interior and exterior climate has been achieved.
EXAMPLE: Commercially available or custom-built stock in which a conscious effort has been made to have a well – constructed case that better isolates the interior environment.

DESCRIPTION OF MATERIALS: The frame is made of painted or varnished wood, or of metal. The panes are made either of glass or of perspex, bearing in mind the diffusion capacity of this material. The number of joins are kept to a minimum to avoid leakage of air, and where they are necessary, such as between the panes and the frame, sealants are used to minimise air exchange.

FUNCTION: ADVANTAGES: may be used to create a microclimate for the object, i.e. a more stable climate to that outside the case. It protects against the entry of dust and pollution in particulate form. It can be undertaken without incurring too much expense and without it becoming labour-intensive.
DISADVANTAGES: Through the reduction of air-exchange between the inside of the case and its ambience, there may be a build-up of acid vapours as breakdown products of degrading materials within the case. Unless these vapours are able to disperse, they will cause the object to deteriorate.

SYMBOL 2.3.   DESCRIPTION

TYPE: Case in which an attempt has been made to reduce air leakage to a minimum.
EXAMPLE: Due to considerable cost in time and money, airtight standard museum cases do not exist. Since there will always be some diffusion through porous construction materials or through joins, this represents the type of case in which the air exchange rate has been consciously reduced to a minimum. Cases described as "hermetically sealed" in the literature, fall into this category.

DESCRIPTION OF MATERIALS: Every material is made of impermeable fabric such as metal for the frame and glass for the panes. The joins and closures are either fused, soldered or welded together permanently using such materials as lead solder. The case may contain either air or an inert gas. The possible inclusion of a leak detector would be evidence that the case is not airtight.

FUNCTION: ADVANTAGES: protects against fluctuating RH by isolating the object within a microclimate within the case. It provides also the surest protection against the effects of dust, dirt, pollution and micro-organisms.

DISADVANTAGES: high cost in terms of time and money. It is therefore feasible only for individual and unique works of art. This type is more applicable to RH control for organic objects rather than for the display of vulnerable metals. The entry of small amounts of air may cause deterioration of materials, the acid breakdown products of which, finding no escape, will accumulate within the case to cause the degradation of the object.

N.B. It should be stated that though attempts had been made in the past to use such cases with the interior under vacuum, it is difficult to maintain this, even over a short period of time, and it has never actually been achieved with a museum case.
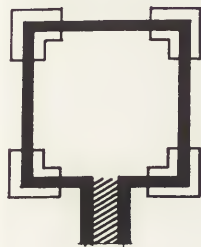
SYMBOL 2.4   DESCRIPTION

TYPE: Case into which air is allowed to enter through one source, usually a hole into which a filter has been placed.
EXAMPLE: due to the conscious decision to allow air exchange between the interior and exterior of the case through one source, leakage of air through joins or porous construction materials is minimised. However, every effort should be made to construct a case similar to 2.3.

DESCRIPTION OF MATERIALS: Similar materials to the case described in 2.3. are used, including the fact that a hole, the diameter of which has been quoted differently by different authors, is constructed. A filter placed inside the hole to eliminate dust and sulphur dioxide, allows only pure air to enter the case.

FUNCTION: ADVANTAGES: does not allow the entry of corrosive vapours which could harm the object, into the case.
DISADVANTAGES: deliberate leakage must be taken into account when a microclimate is being set up, and allowance made for the change it may cause. Consequently it may complicate calculations of quantities of buffering materials. It may prevent entry of corrosive vapours, but it does nothing to actively dispell those vapours that have accumulated in the case from the materials used. It may be labour-intensive and expensive to construct.

In concluding section 2, it can be stated that, for Symbol 2.1., the climate inside and outside the case would at any one time be similar. In Symbols 2.2., 2.3., and 2.4., however, the establishment of microclimates in these cases, seems more feasible than in 2.1. Taking into consideration such variables as ambient conditions, case materials, quantity of buffering agent and mass of object, the length of the half-life of such a microclimate may be extended depending on the requirements of the display. As an example, reference is made to Garry Thomson, "RH Stabilisation in Exhibition Cases - Hygrometric Half-Time", in Studies in Conservation, 22, 1977, where calculations of the quantity of buffering agent for a micro-climate are made.

3.   CONTROLLED CLIMATE SYSTEMS FOR DISPLAY CASES

The macroclimate and microclimate systems described below, have been extracted from the literature, and exemplify the more sought-after trends for the control of the environment within a display case:

3.I   MACROCLIMATE: MECHANICAL SYSTEMS

SYMBOL 3.I.A

DESCRIPTION

TYPE: Air-conditioning plant to control the general gallery climate.

FUNCTION: ADVANTAGES: This system should not only control Relative Humidity and Temperature, but should also filter gaseous pollutants and dirt. (Unfortunately, this is not always the case.) It is however, the complete answer to environmental control.
DISADVANTAGES: The more obvious disadvantages of this system are cost, maintenance and that it is a measure which cannot be undertaken quickly.

N.B. This system will not be given extensive consideration in this paper, which concentrates primarily on microclimate control.

SYMBOL 3.I.B.
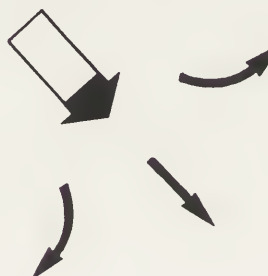
DESCRIPTION

TYPE: Air-conditioning plant which first forces conditioned air through a case before circulating it into the gallery.

FUNCTION: ADVANTAGES: ensures that conditioned air goes through the case and then outwards under pressure. Dust, dirt and pollutants are unable to effect the object by entering the case. This system is better adapted for use with several wall cases.
DISADVANTAGES: has similar cost, maintenance and lack of reliability in terms of breakdown, as 3.I.A. It does not allow flexibility in display layout, which however, 3.I.A. does have.

3.II   MICROCLIMATE: EXTERNAL CONTROL

SYMBOL 3.II.C.

DESCRIPTION

TYPE: dehumidifier or humidifier system attached to one or a small number of cases to control the microclimate within the cases without effecting gallery conditions.

FUNCTION: ADVANTAGES: can be installed quickly in case of emergency. It allows for flexible use with either one or several cases. It does not have high installation or maintenance costs. DISADVANTAGES: subject to breakdown, due to the fact that it is a mechanical system. It may not be a sensitive enough system within the Relative Humidity and Temerature range required.

MICROCLIMATE: INTERNAL CONTROL

SYMBOL 3.II.D.
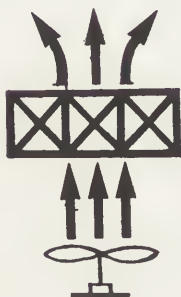
DESCRIPTION

TYPE: Dynamic buffering system, using hygroscopic materials such as silica gel or saturated salt solutions, to ballast fluctuations in humidity. This system includes a fan to circulate the conditioned air which could either have had the moisture-content increased or reduced.

FUNCTION: ADVANTAGES: functions as an independent system within the case. This is a simple system which requires little maintenance. Inclusion of a fan prevents the formation of pockets of stagnant air within the case. DISADVANTAGES: breakdown of the fan may cause the malfunction of the system especially if the buffering agent has not been well distributed within the cause, by causing uneven humidity levels to form.

SYMBOL 3.II.E.

DESCRIPTION

TYPE: a simplified form of the dynamic buffering system described in 3.II.D.

FUNCTION: ADVANTAGES: static system of control of humidity excludes the fan which is subject to malfunction. This is a simple and effective system of microclimate control which works independent of but taking into consideration, gallery conditions. It is inexpensive and can run itself with the minimum of attention. DISADVANTAGES: Unless all the variables are considered carefully before installing such a static system of microclimate control, the special climate established, will soon drift towards gallery conditions.

4.   DISCUSSION

When the need for a form of climate control in a museum, has been identified, a decision has to be made primarily between the use of either a macro- or a microclimatically controlled system. The choice depends of a number of factors, namely, finance, time available, urgency of the problem, size of the collection requiring attention, and

the co-operation, knowledge and interest of the personnel recommending, approving and finally, undertaking the task. If microclimate control of individual or groups of cases is selected, the choice of internal or external, static or dynamic control of climate should next be considered. Consequently, it is not only misleading but also dangerous to generalise by suggesting one system instead of another, for given sets of circumstances. Recommendations may be made only after each individual case has been assessed because arguments both in favour of and against, the use of any of these systems, can be made.

5.   A TYPOLOGY OF MUSEUM DISPLAY CASES AND CLIMATE CONTROL SYSTEMS

The controlled climate systems which have been listed and explained in 3., may be used either individually, or in varied combination, with any one of the four museum display cases described in 2.

Tabulated below, is a typology which links together climate control systems and display case types in an effort to standardise terminology.

The climate control systems discussed are listed in the table, along the vertical axis, while the different types of museum display cases are arranged along the horizontal axis. By reading along both axes, line diagrams of different climate/case combinations may be located. Each combination is illustrated by examples which have been reported after experiment, trial and use. These examples have been listed underneath the table.

It will be seen from an initial glance at the table, that not all the available spaces have been filled. This is because, not all methods of climate control can be effectively or even sensibly used with any type of case construction. Consequently, only the more practical combinations have been tabulated. Where a question mark has been placed in a space, no example has been found through a search in the literature. This does not mean that such an example has not been attempted. In fact, any suggestions or information to modify or complete the table would be greatly appreciated.

It can be seen from an examination of the table and the examples which support it, that microclimate control seems to have been attempted, not surprisingly, in museum cases in which a reduction of the exchange of air between the interior and the exterior climate has been achieved (2.2.).

The air-conditioning of museum galleries however, is still a common occurrence (3.I.A.), and a variety of museum cases have actually been used in these conditions (1:A.,2:A.,3:A.).

Two other factors require mention. An example has been found of the use of a case into which air is allowed to enter through one source usually a hole into which a filter has been placed (2.4.). This is the ventilated case for the Raphael Cartoons at the Victoria and Albert Museum in London which is a static system which employs active carbon filtration. This example has not been included in the table because the gallery conditions do not correspond to any of those listed below.

Though the creation of a microclimate within a case in which there is free air exchange between the inside of the case and ambient gallery conditions (2.1) is a waste of time, money and effort, yet without actually knowing of any examples, it seems very likely that it has been done, and is still being done. Unfortunately this shows a lack of understanding of the basic principles of Climate Control in Museums.

Although this scheme has been devised for the control of Relative Humidity in museum display cases, a similar Table to include different lighting systems used in museums , can also be plotted.

TABLE FOR STANDARDISATION OF MUSEUM DISPLAY CASES AND CLIMATE CONTROL SYSTEMS

	DISPLAY CASE 2.1	DISPLAY CASE 2.2	DISPLAY CASE 2.3	DISPLAY CASE 2.4
MACRO-CLIMATE 3.I A	1:A	2:A	3:A	?
MACRO-CLIMATE 3.I B	1:B	2:B		
MICRO-CLIMATE 3.II C		2:C	3:C	
MICRO-CLIMATE 3.II D		2:D	?	?
MICRO-CLIMATE 3.II E	1:E	2:E	3:E	?

EXAMPLES FROM THE LITERATURE IN SUPPORT OF THE STANDARDISATION OF TERMINOLOGY TABLE

1:A Vast majority of museums with air-conditioned galleries have this type of case construction.

1:B Metropolitan Museum of Art – Egyptian Galleries (Phase I): Stolow, N., "The Microclimate: A Localised Solution", in Museum News, 56, 1977, pp.60–61.

1:C Combination of climate and case unlikely to exist.

1:D Combination of climate and case unlikely to exist.

1:E Most museum cases in which an attempt has been made to create a microclimate without actually understanding the limitations of the system.

2:A Large number of museums with air conditioned galleries have this type of case construction.

2:B Michalski, S., "A Control Module for Relative Humidity in Display Cases", in Science and Technology in the Service of Conservation, Preprints of the IIC Washington Congress, 1982.

2:C Museum of Mankind, The Ethnographic Department of the British Museum, London: Temporary Exhibition on Mexican Art, 1971.

2:D Organ,R.H., "The Safe Storage of Unstable Glass", in The Museum Journal, 56, April 1956–March 1957.

2:E Ramer, B.L., "Stabilising RH Variations within Display Cases: The Role of Silica Gel and Case Design", in ICOM Committee for Conservation, 6th Triennial Meeting, Ottawa, 1981.

3:A Metropolitan Museum of Art - Egyptian Galleries
(Phase III). Currently under construction.

3:B Combination of Climate and Case unlikely to exist.

3:C British Museum cases for Unstable Metal Objects:
Thomson, G., The Museum Environment,
Butterworths: London, 1978.

3:D   – Literature or personal discussion have
failed to reveal the use of this combination of climate
and case.

3:E Miura, S., "Control of Climate in a Showcase by
means of Zeolite: Report on the Exhibition of
'La Joconde', in ICCROM Conference on Museum
Conservation Climate, Rome, 1978.

4:A   – Literature or personal discussion have
failed to reveal the use of this combination of climate
and case.

4:B Combination of climate and case unlikely to exist.

4:C Combination of climate and case unlikely to exist.

4:D   – Literature or personal discussion have
failed to reveal the use of this combination of climate
and case.

4:E   – Litersture or personal discussion have
failed to reveal the use of this combination of climate
and case.

ACKNOWLEDGEMENTS

THE EFFECT OF ILLUMINATION ON THE APPEARANCE OF MUSEUM OBJECTS

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ABSTRACT

Several theoretical models are reviewed for
their relevance to problems associated with
the perception of museum objects under
different lighting conditions. Some of the
principle results are outlined in two
examples. It is concluded that there are
significant benefits to be achieved from a
detailed study of the interaction of light
with objects, but that more analysis of
specific situations must be carried out before
general conclusions can be drawn.

INTRODUCTION

In this paper I want to develop the idea that
good museum lighting depends upon a detailed
consideration of the interaction of light with
objects.

Much has been written about the degradative
aspects of light and the need for low levels
of illumination and U.V. Again, there is
plenty of literature on perception, which we
can go to to understand why we need good
colour rendering or un-distracting wall
colours. However, there is little readily
available information for the conservator on
the physical interaction of light with objects
with respect to how they reflect light.

Although there are a number of papers which
have examined pigment optics, they have in the
main been studies of fading or the principles
of I.R. reflectography. I want to present
here a brief review of the theoretical
treatments of pigment optics, but with direct
reference to how that object then appears to
us. This is with the intention of showing how
lighting arrangement will significantly alter
an object's appearance. I shall, therefore,
be treating objects as optical 'instruments',
showing how light interacts with them in
precisely definable ways.

After developing the theoretical treatments
necessary by considering the optical
'components' of an object, we shall be able to
see which parameters are related to illumina-
tion. These will basically be seen to relate
to quantities like diffuseness, angle of
illumination, and polarisation.

Although I am concentrating on the physics of
the situation, it must be stated before
proceeding that the significance of some of
the effects that I shall describe ultimately
rests on the nature of our perception, as to
whether we can see them. However, these
differences exist whether we can see them or
not, so the physical relationship of
illuminant, object and observer must be the
starting point.

Objects as optical devices.

We can perhaps broadly define the appearance of
an object in terms of four aspects relating to
that object. Of primary importance will be
the physical form - its shape. Analytically its
effect is purely geometric (the spatial
relationship between object and observer).
Secondly the appearance will depend on colour,
that is the selective proportional reflection
of light by wavelength. Thirdly surface
characteristics not directly relating to the
gross physical form such as texture (eg wood-
grain) or gloss. These will affect the amount
of diffusion of incident light. Exactly what
should be included as such depends on the
resolution of the eye (consider canvas texture
from a distance). Finally we must include any
visible layer structure to an object such as
paint glazes or embedded decoration in glass.
Again although principally we perceive this by
changes in spatial orientation, the ability to
relate reflected light to different layers,
say in a paint structure is important. For
example, surface reflections from a varnished
painting are not associated with the underlying
colours, although light from both leaves from
the picture's surface.

For a mathematical treatment these categories
can prove awkward, and for a simple reason.
It is more satisfactory to proceed by studying
underlying physical processes which affect the
reflection of light. In this way we find that
there is a more elegant articulation to our
problem.

We can divide our object up into either layers
or boundaries, solving general equations for
specific cases. As an example of this I shall
mention a model that I will talk about in more
detail later, the Mie theory, which describes
the interaction of light with pigment particles
in a paint film. Part of the theory describes
the scattering power of a particle, expressing
in a single function three aspects: reflection,
refraction and diffraction. Any particle will
do all three, and in an interelated manner.
We understand the processes separately, but
the complete description of them is a function
of the particle, the parameters interacting in
a not immediately apprehendable way. Using a
mathematical language we can solve problems
that we could not argue out verbally.

The theories or models that I am about to
present are, therefore, mathematical
articulations of the process of electro-
magnetic scattering, basically for different
types of boundary: either surfaces that are
planar, or for spherical particle surfaces.
We shall see that there are two ways of
solving our problem; by considering light as
diffusing through the substance of an object,
or by solving Maxwell's equations (which
describe light waves and the way they travel)
at boundaries and around particles.

Scattering of light

Probably the only familiar treatment of the
interaction of light with objects is the
Kubelka-Munk two-flux model for paint films.
It has been used to much effect in, for
example, evaluating the ideal conditions for
I.R. reflectography, and studying the
penetration of radiation into paint films, and
in describing the 'fading' of colours in
paintings.

However, it has a number of drawbacks. These
are as a result of the simplifying assumptions
on which the Kubelka-Munk equations are based -
which unfortunately eliminate parameters we
are interested in, such as the diffuseness of
the incident light. Therefore I now want to
introduce the theory from which the Kubelka-

Munk model dervies - Radiative Transfer
theory.

Radiative transfer theory was originally
developed to examine the problem of how light
from distant galaxys and stars reaches us. It
is a theory that considers the diffusion of
light through a medium; one which absorbs,
emits and scatters radiation. So it has
premises which are entirely general and
arbitrary. From this an 'equation of
transfer' is produced and solved for a
particular set of circumstances. For example
the Kubelka-Munk theory takes diffuse incident
light and considers its interaction with
finite or semi-infinite (optically) plane-
parallel layers, but,as I indicated, the
equation of transfer could be set up and
solved for any circumstance. This has been
done for a number of situations, two of which
I want to mention here.

The equation of transfer was first solved
completely in the 1940's by Chandrasekhar, who
also developed several applications 1 . In
particular he solved the problem of scattering
by planetary atmospheres, which importantly
gives us a very complete description of the
illumination from sunlight at the earth's
surface. The applications of this are obvious
if you consider the problem of natural
(daylight)illumination in a gallery.

Because of the complexity of the solution
involved, more specific cases than that
treated by Chandrasekhar have been solved by
computer and produced as numerical tables 2 .
I want to mention one such set of tables,
where the luminance of an arbitrary object (a
white sphere) has been computed for different
inclinations of the sun. The authors
specifically mention the applicability of
their tables to the museum situation.

I hope that two points are now clear about
Radiative Transfer theory. First, that it is
a very flexible model, but that it needs to be
developed for specific requirements. It will
though, give us the results we want to know -
how some defined light source will interact
with an object. Second, the equation of
transfer is solved on the basis of considering
layers. This is what makes the Kubelka-Munk
treatment of paint films so straightforward.
However, there is a necessary drawback in this,
because the solution demands the consideration
of more-or-less homogeneous layers. It would
be difficult if we were trying to treat
textiles in this way.

This brings us on to the other approach to the
problem.

There are two specific solutions to the light-
scattering problem that I want to discuss.
Mie theory is the mathematical treatment of
electromagnetic scattering by particles, where
the particle shape is essentially arbitrary.
Particle shapes could be roughly spherical,
like many pigment particles are, or
cylindrical as with fibres. Fresnel's
equations on the other hand, are solutions of
the mathematics describing electromagnetic
scattering from boundaries between media of
different refractive index.

Problems involving non-planarity of such
boundaries can be circumvented using
statistical techniques, a subject that I shall
come back to.

These two models are more suited to dealing
with the complexities of an object where there
is a natural inhomogenity. Mie theory avoids
the disadvantages of the flux-based Radiative
Transfer theory by starting with the particle
and then working up towards the bulk property

of reflectance.

Although necessarily complex in application,
the value of Mie theory probably lies in its
application to the analysis of problems such
as how to minimise the visual distraction of
nets sewn over textiles (a conservation
technique for supporting degraded fabric).
The Mie treatment of regular or ordered
structures such as nets is relatively straight-
forward. In the introduction I separated out
the effects of surface reflection or gloss,
and visible layer structures. These are not
separable theoretically as they are the same
physical process. Any difference lies in
either the total reflected flux from boundary
(whereas 4% of the incident light is reflected
by the surface, only 0.1% might be reflected
from a boundary within a paint film), or in
our perception of where these reflections lie
within the structure.

Fresnel's equations have, therefore,
considerable importance. These equations are
the exact solution of how light is reflected
(and refracted and transmitted) by a boundary
between two media. We are normally only aware
of the surface reflections from objects, but
any complete description of reflectance treats
internal boundaries as well. It should be
noted that gloss or surface texture only
affects the distribution of the reflected
light, the total reflectance always being
given by Fresnel's equations. This gives an
interesting result.

Because the total reflected light from a
boundary is independant of the nature of that
surface (or rather being only a function of
the relative refractive index) we can say
immediately what the effect of different
illumination will be.

In addition to R.I. there are two other
variables involved in determining the boundary
reflectance which relate specifically to the
illuminant: the polarisation and the
diffuseness. Knowing these factors and
integrating over the appropriate angles of
illumination will give the amount of light
reflected. This approach could be taken to
evaluate how much surface glare there would be
in a variety of lighting conditions.

Practical examples

To illustrate more fully the kind of
information that we can expect to get from
these methods of analysis I have chosen two
examples which explore the optical inter-
actions when i) Light strikes the surface of a
painting, and ii) How fibres reflect light.

Case i) is a more realistic treatment of the
problem that I have just discussed. The
boundary between paint or varnish and air will
reflect a proportion of the incident light
according to Fresnel's equations. Further, if
the painting's surface was optically smooth,
the angle of reflection would be equal to the
angle of incidence. But the surface will have
roughness, and the light will be scattered.
To treat this situation we need additional
information - knowledge of the way in which
the surface is rough. At any point, the
interactions will be identical to those
outlined above - surface roughness simply
presents a range of orientations of that
surface.

Using the measured statistical distribution of
the surface roughness, it is then possible to
calculate the proportion of the light
reflected into any angle. The computation may
then explore the effect of different illuminant
and observe parameters.

My second example, which uses the approach of
Mie theory to examine the way fibres scatter
light, was partly chosen because there already
exists some literature on the subject, 3, 4
and for the details I would refer you to those.
The other reason was that fibres constitute a
wide range of museum objects (most notably
prints and drawings, and textiles).

The analysis will begin by giving a set of
values: absorption, and scattering at various
angles. The next stage is to calculate the
effect of large numbers of these scattering
fibres together - multiple scattering. For a
particular object there will then be
restrictions on fibre orietation, such as with
paper where fibres are randomly orientated in
two dimensions, or textiles, where there is
the further restriction of warp and weft. All
these parameters must be accounted for in what
becomes, it must be admitted, a rather complex
equation. However, this approach was
introduced to handle the complexities of a
real situation, and this is what it will give.
Calculations must be on a specific problem,
and may be lengthy - but it is possible to
explore the effects of all illumination
variables. Principally one would be concerned
with the ultimate distribution of reflected
light.

Conclusion

My intention in discussing these theoretical
treatments has been to show that there are
certain specific variables involved in the
interaction between light and an object, and
that their effect can be precisely determined.
Although the ultimate significance of these
effects rests on our perception, it is surely
essential to a rigorous evaluation of museum
lighting that we know the primary stimulus to
our visual system. Therefore, my objective has
been two-fold. Firstly to show some of the
powerful techniques available for the analysis
of optical action in a complex structure; and
secondly to elucidate the variables involved
which relate to illumination. It is of course
difficult to talk about specific conclusions.
Effects are highly object dependant, so that
particular cases must be solved. There is much
to be gained from the experience of analysing
a wide range of situations, and we can look
forward to the benefits of this experience in
the future.

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CONTROLE DU CLIMAT AUTOUR DE 197 INSTRUMENTS DE MUSIQUE

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SUMMARY

The relative humidity surrounding 197 musical instruments, 84 of which were string instruments including several Stradivarius, was stablized inside 38 showcases. 13 quintals of silica gel were used for this purpose. The relative humidity was monitored constantly during the last four years and recordings show that variations never exceeded 2% daily, 4% monthly and 7% yearly. The silica gel was not modified in any way during this time.

En 1979, un comité présidé par le prof. F. Rossi et groupant les quatre Rotary Club florentins décida de promouvoir une exposition temporaire des instruments de musique du Conservatoire de musique Luigi Cherubini de Florence. Du fait de la fermeture pour travaux en 1964 du Musée du Conservatoire, ces instruments étaient conservés depuis dans trois salles de réserves sans chauffage et situées au centre d'un bâtiment ancien. De ce fait, les conditions climatiques subissaient un cycle de variations lentes annuelles allant de 14° à 29°C et de 45% à 59% humidité relative. Les instruments les plus sensibles se trouvaient dans une salle où l'humidité relative variait de 50% à 55% avec un moyenne annuelle de 53,5% (fig. 1).

Les collections étaient en très bon état de conservation. Il fut donc décidé de porter une attention toute spéciale au maintien de la stabilité de l'humidité relative durant le transport de la collection des réserves jusqu'au lieu d'exposition, durant la durée d'exposition et pendant le transport de retour.

Les collections

L'ensemble qui devait être exposé était composé de 197 instruments dont 84 à cordes. Il comprenait entre autres le premier pianoforte vertical construit par Domencio del Mela en 1739, l'épinette construite par Benedicti Floriani en 1568, et le violoncelle et la "Viola Medicea" construits par Antonio Stradivarius en 1690 pour le Prince Ferdinando de Medici, fils de Cosme III. Ce dernier instrument est d'une importance exceptionnelle puisqu'il n'a pas subi au XIXe siècle les modifications qui furent apportées alors à presque tous les instruments de son type (fig. 2).
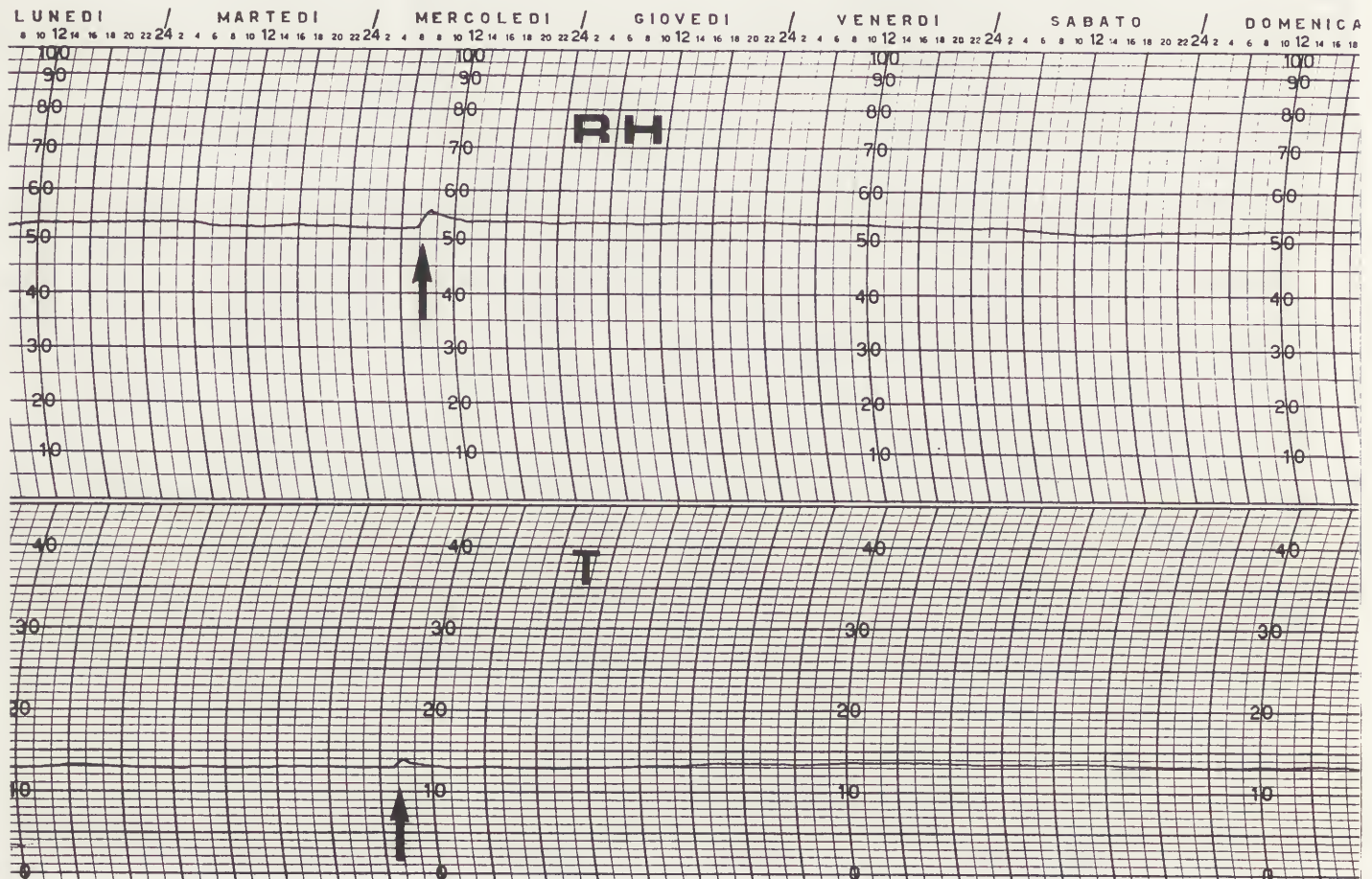

Fig. 1 Conditions climatiques dans les magasins au mois de janvier 1980. Noter l'influence de l'ouverture des portes.

Fig. 2 "Viola Medicea" construite par Stradivarius pour Ferdinand de Medici.

Sensibilité des violons aux variations d'humidité relative

Qui a assisté à un concert a certainement observé que les instruments à cordes étaient maintenus dans la salle durant l'entracte et que les musiciens rectifiaient souvent l'accord de leur instrument.

Cela est dû à la grande vulnérabilité des instruments à corde aux variations d'humidité relative. Ils sont en effet composés de matériaux organiques très variés (1). Dans un violon (fig. 3), par exemple, la table d'harmonie, l'âme sont en essence résineuses (sapin); le fond, les éclisses, le manche et la volute sont en érable; le chevalet est en platane; la touche, la cordière et le bouton sont en ébène africain.

Le manche décoré de sa volute et la caisse forment le violon proprement dit auquel s'ajoutent les accessoires vitaux - âme et chevalet - qui ne sont pas collés pour permettre la vibration de l'instrument.

L'ensemble tient par les cordes mises sous tension (30 kg environ)(2). Les cordes des instruments anciens étaient faites d'intestins de mouton. Aujourd'hui, ces cordes sont encore faites de boyaux; certaines sont revêtus de métal.

Si l'humidité relative augmente les cordes se détendent légèrement, le chevalet tombe et l'âme peut se déplacer. Si l'humidité relative s'abaisse les cordes se tendent et, soit se rompent, soit risquent d'endommager la table d'harmonie.

Il est donc nécessaire d'exposer les violons et tous les instruments à cordes avec celles-ci tendues, accordées et de maintenir l'humidité relative aussi stable que possible.

F. Hellwig propose une humidité relative de 55%(3).

Recherches faites pour maintenir l'humidité relative

L'exposition devait se tenir de février 1980 à février 1981 dans quatre salles du deuxième étage du Palais Pitti exposées au nord-ouest. Elles n'étaient pas climatisées et étaient chauffées en hiver par une série de radiateurs électriques mobiles. La plus grande avait une surface de 160 m^2 et une hauteur de 12 m. On ne possédait aucun enregistrement de conditions climatiques de ces salles.

Il fut décidé d'installer un système d'air conditionné. L'étude fut faite par la maison de Micheli. Rapidement il fut décidé de renoncer à installer l'air conditionné pour les raisons suivantes:

1) Les installations électriques du Palais Pitti n'étaient pas assez puissantes pour permettre le branchement des six unités nécessaires pour conditionner l'air. Il aurait donc fallu installer une cabine spéciale d'électricité ce qui était difficile dans le centre historique.

2) Pour épargner l'énergie la compagnie d'électricité prévoyait des coupures de courant trois heures tous les mercredis matins.

3) Le devis minimum total pour l'installation était d'environ 110 million de lires sans compter le fonctionnement.

4) Il eut été impossible d'ouvrir les fenêtres sur les jardins de Boboli entourant le Palais.

Pour ces quatre raisons majeures il fut décidé d'étudier la possibilité de contrôler l'humidité relative au moyen de produits tampon seulement à l'intérieur des vitrines et de laisser fluctuer le climat à l'intérieur des salles. Les instruments ayant été maintenus à une humidité relative de 53,5%, il était évident que l'H.R. dans les vitrines devait s'approcher le plus possible de 53,5%.

1. table d'harmonie
2. âme
3. fond
4. éclisses
5. manche
6. volute
7. chevalet
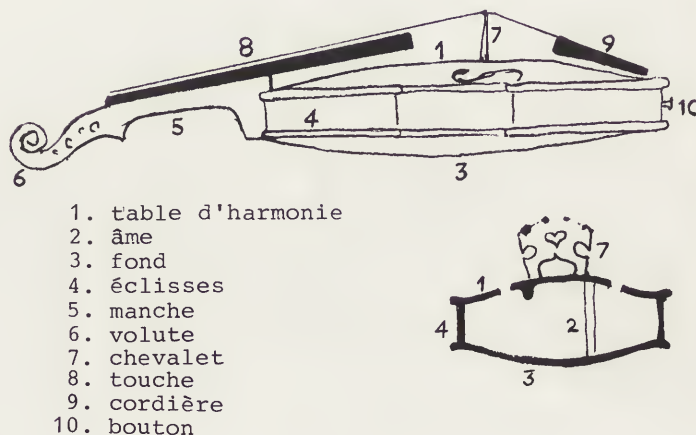8. touche
9. cordière
10. bouton

Fig. 3 Dessin et section d'un violon.

Une vitrine expérimentale (fig. 4) avec double fond fut construite par la maison San Benedetto de Florence. Les caractéristiques en étaient les suivantes:

Longueur: 1,60 m
Largeur: 0,80 m
Hauteur: 1,40 m plus 50 cm de pieds
Volume: 1,7 m3
Verres doubles athermiques; 5 mm verre + 9 mm air + 5 mm verre
Eclairage: extérieur
Structure portante: en acier avec peinture emaillée de couleur jaune-or
Panneau séparant la vitrine du double fond (pour contenir le gel de silice): 1,60 x 0,80 x 0,12 m
Double fond: masonite percé de 84 trous de 0,5 cm de diamètre
Prix de la vitrine: 1.028.000 lires (4) dont deux tiers pour la partie métallique et un tiers pour le double verre.
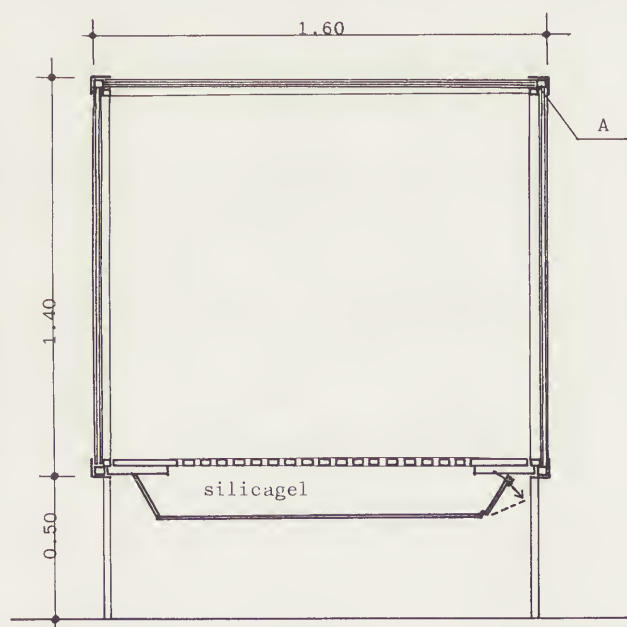

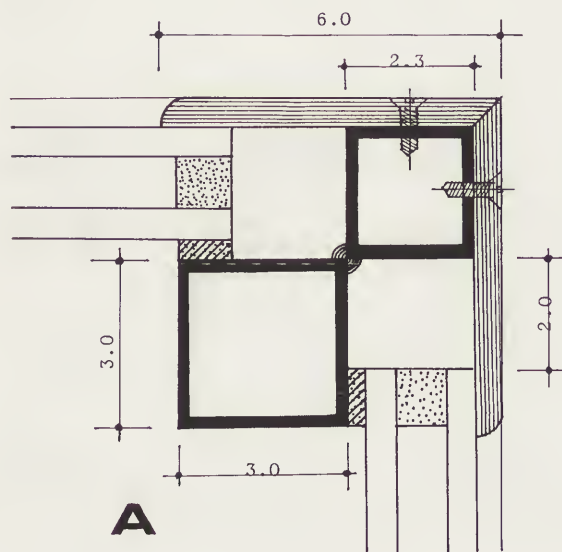Fig. 4 Plan de la vitrine expérimentale.

Fig. 5 Détail d'un montant.

Le produit tampon choisi avait les caractéristiques suivants:

Produit : gel de silice
Producteur: Grace Italiana S.p.A.
Référence: NATO MIL 3464
Quantité: 34 kg en sachets de 480 g, soit 20 kg par m3 de vitrine.(5)
Prix du gel de silice: 130.000 lires

Une attention particulière fut portée pour assurer l'étancheité de la vitrine. Les parois en verre étaient appliqués au moyen de vis au chassis métallique (fig. 5).

L'étude dura quatre mois dont trois mois dans les futures salles d'exposition (6). Les variations climatiques étaient enregistrées au moyen de trois thermo-hygrographes mensuels type MT 1520 de la maison S.I.A.P. à Bologne. Un des appareils étaient placés à l'extérieur de la salle, un sur la vitrine, un à l'intérieur de la vitrine. Les 34 kg de gel de silice furent équilibrés à 53% dans la chambre ambientale de la maison SIEME.

Le gel de silice fut placé dans le double fond de la vitrine. Durant les quatre mois d'étude, en dépit du verre athermique les variations journalières de température de 4°C enregistrées dans la salles étaient transmises quasi intégralement à l'intérieur de la vitrine avec un décalage de deux ou trois heures. Par contre, l'humidité relative à l'intérieur de la vitrine est restée remarquablement stable variant d'abord de 6% par semaine puis de 2% au maximum lorsque l'étancheité fut améliorée au moyen de joint au silicone. Il est à noter que les variations extérieures atteignaient 30%.

Devant ces résultats inespérés il fut donc décidé d'utiliser le gel de silice pour stabiliser l'humidité relative autour des instruments exposés. 37 vitrines supplémentaires furent commandées pour un prix total de 39.000.000 Lit.

Equilibrage du gel de silice

Les 38 vitrines représentaient un volume d'environ 60m3. Il fut donc acheté 1230 kg de gel de silice (coût 4.300.000 Lit.) qui durent être conditionnés à 53%.

Au sortir de l'usine le gel de silice est vendu sec - soit équilibré à 0% d'humidité relative. Il fallait donc l'humidifier pour le porter à 53%, ce qui représente, pour le type de gel employé, une addition d'environ 300 g de vapeur d'eau par kg de gel de silice sec. Pour accélérer le processus, dans un premier temps on pulvérisa environ 250 g de vapeur d'eau par kg de gel silice sec. Puis le gel silice fut porté dans une chambre ambientale d'un volume de 27m3 environ ˙(3m x 3m x 3m) dans laquelle régnait une humidité relative de 53%. Il fallut 96 heures pour que le gel de silice, absorbant la vapeur d'eau de l'air ambiant, vienne s'équilibrer à 53%. Le gel de silice fut alors mis dans des tonneaux hermétiques et transporté dans les réserves où les instruments étaient conservés à 53%. Les tonneaux furent ouverts.

Nous avions maintenant les instruments, l'air et le gel de silice au même niveau d'humidité relative.

Transport des instruments

Huit jours plus tard, soit dix jours avant l'inauguration de l'exposition, 600 kg de gel de silice furent prélevés des réserves et transportés en tonneaux scellés au Palais Pitti et insérés dans le double fond des vitrines, recréant ainsi dans la vitrine l'humidité relative de 53% semblable à celle qui régnait dans les réserves.

Les vitrines étaient maintenant prêtes à recevoir les instruments.

Sept jours avant l'inauguration de l'exposition, le transport et l'installation des instruments débuta. Les instruments devaient être transportés d'un bout à l'autre de la Ville de Florence sur les deux kilomètres séparant le Conservatoire Luigi Cherubini du Palais Pitti. Des caisses spéciales en bois avaient été réalisées par l'Ecole de Lutherie de Crémone (7) et ces caisses avaient été elle-mêmes portées précédemment à une humidité relative de 53% dans une chambre climatique pendant trois jours. Les instruments furent placés dans leurs caisses respectives avec les 630 kg de gel de silice restés dans les réserves. Ces caisses furent alors portées au Palais Pitti et les instruments furent rapidement installés dans leurs vitrines et le gel de silice ayant servi pour le transport fut alors ajouté à celui déjà présent dans le double fond de la vitrine. Il régnait dans la salle au moment du transport une humidité relative moyenne de 57%

Mesures des variations climatiques durant l'exposition

Dans chacune des 38 vitrines il y avait un hygromètre et un thermomètre.

Une vitrine fut choisie comme vitrine représentative sur laquelle on installa un thermohygrographe mensuel SIAP MT 1520 et dans laquelle on installa un thermo-hygrographe similaire (fig. 6).

Cette vitrine ne contenait que des instruments en cuivre - trompette, cor, etc. - ce qui n'obligeait pas à maintenir un climat parfaitement stable et autorisait donc l'ouverture mensuel pour remonter le thermo-hygrographe. Cette vitrine était de plus la plus exposée près des fenêtres et dans un passage ce qui correspondait à la zone climatique la moins stable.

Les résultats obtenus au cours des 12 mois d'exposition sont indiqués au tableau N. 1. Durant cette année, on n'a jamais observé à l'intérieur des vitrines des variations d'humidité relative journalières supérieures à 2%.

De toutes les enregistrements réalisés, il est présenté ici, à titre indicatif, ceux realisés à l'extérieur de la salle, dans celle-ci et dans une vitrine durant le mois d'octobre (fig. 7).

Afin de contrôler l'influence du gel de silice dans la stabilisation de l'humidité relative, durant le mois de septembre le gel
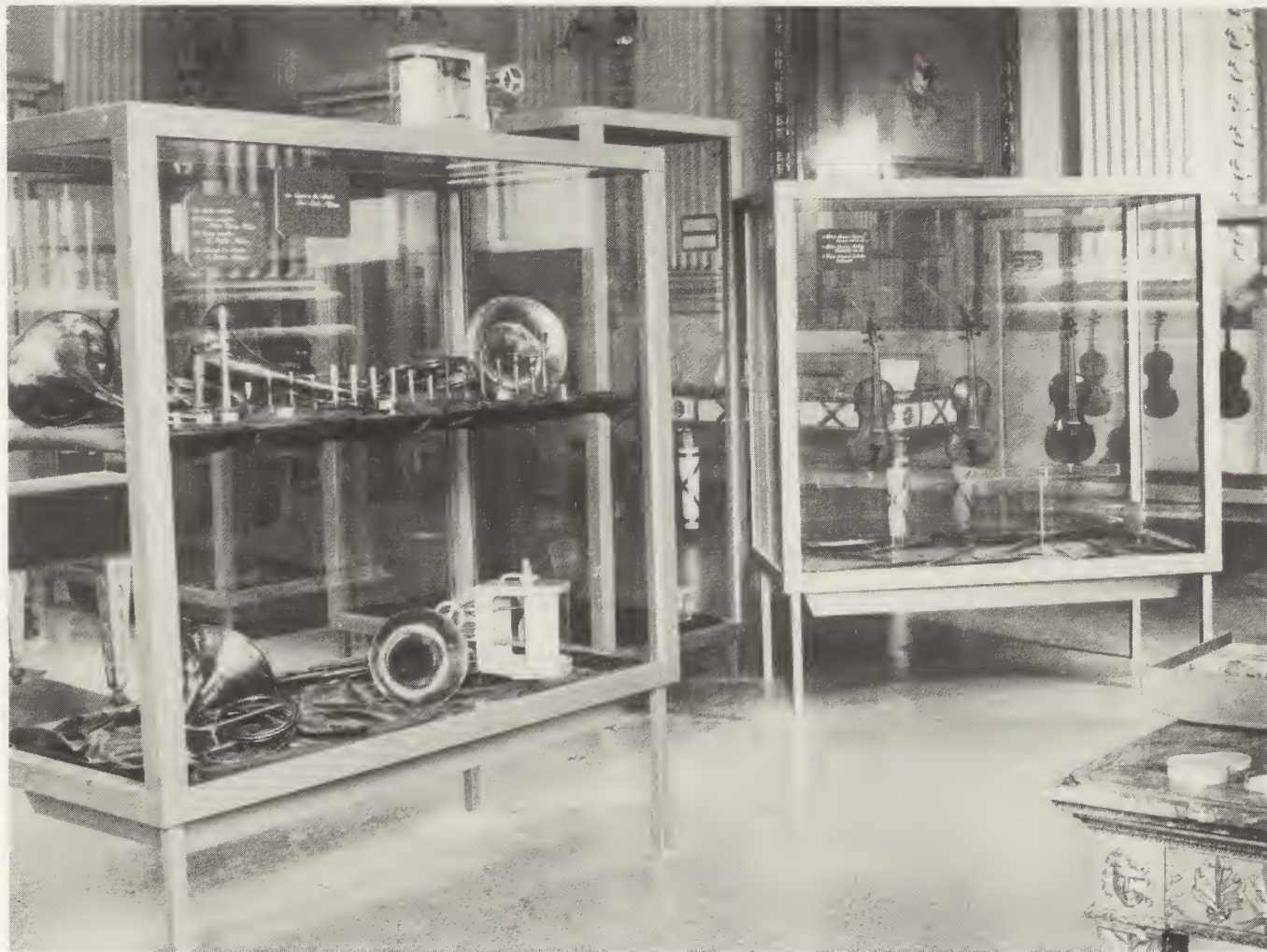

Fig. 6   Vitrine "témoin" contenant des instruments métalliques, sur et dans laquelle se trouvent les appareils enregistreurs.

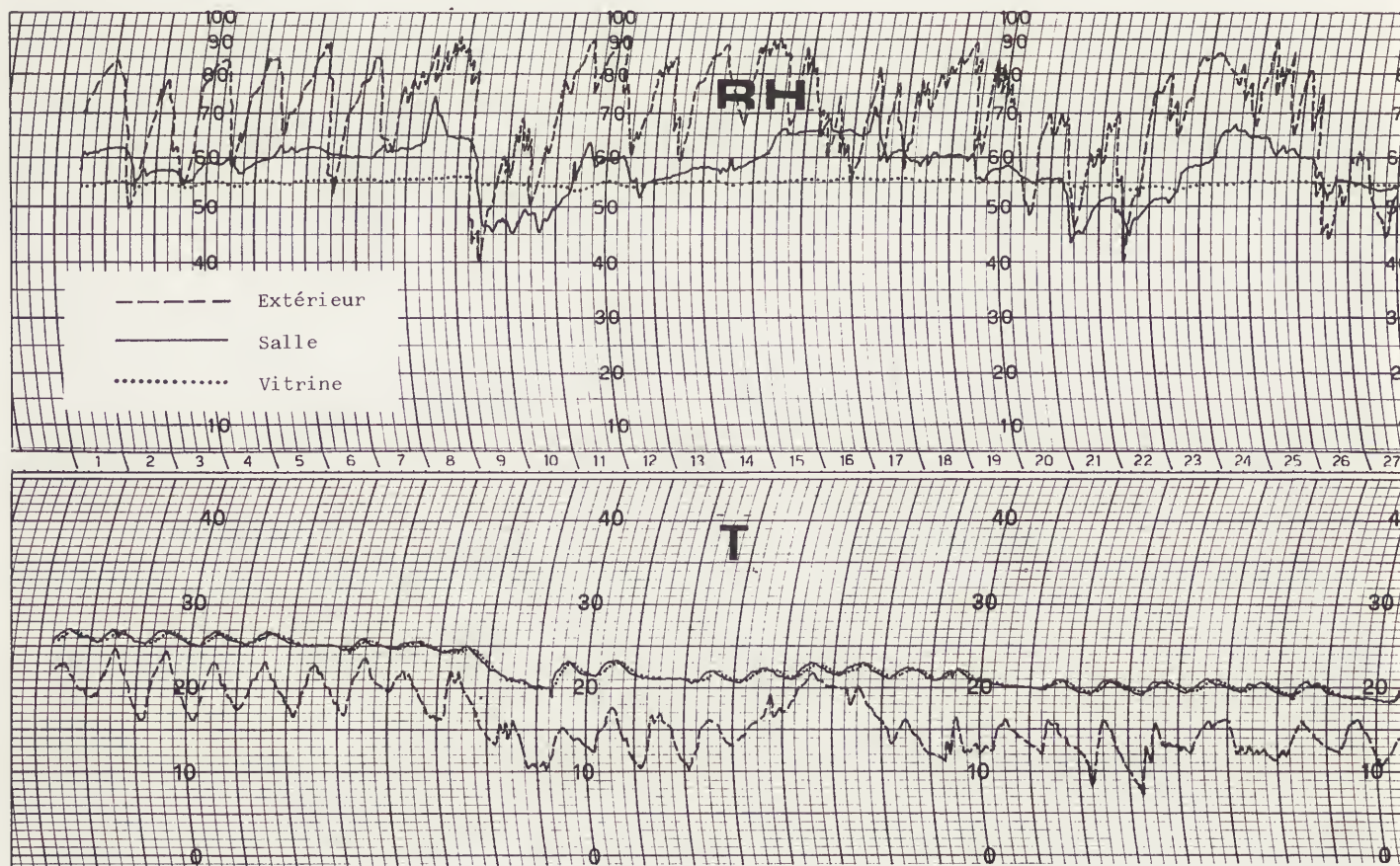|		Extérieur	Salle	Vitrine
365 jours 1980	Température Minim-Maxim.	-7°C -- 36°C (10.2.81) (2.8.80)	4°C -- 32°C (13.1.81) (2.8.80)	8°C -- 31°C (10.1.81) (2.8.80)
	H.R. Minim-Maxim.	4% -- 100% (26.2.80) (---)	27% -- 86% (22.7.80) (16.12.80)	51% -- 56% (--) (--)
30 jours Oct. 1980	Température Minim-Maxim.	7°C -- 25°C	18°C -- 27°C	19°C -- 27°C
	H.R. Minim-Maxim.	40% -- 91%	45% -- 75%	53% -- 56%
24 heures 9/10/80	Température Minim-Maxim.	15°C -- 22°C	23°C -- 25°C	23°C -- 25°C
	H.R. Minim-Maxim.	40% -- 87%	45% -- 64%	54% -- 55%

Fig. 7 Variations des conditions climatiques durant octobre 1980 hors de la salle du Palais Pitti, dans celle-ci et dans la vitrine témoin.
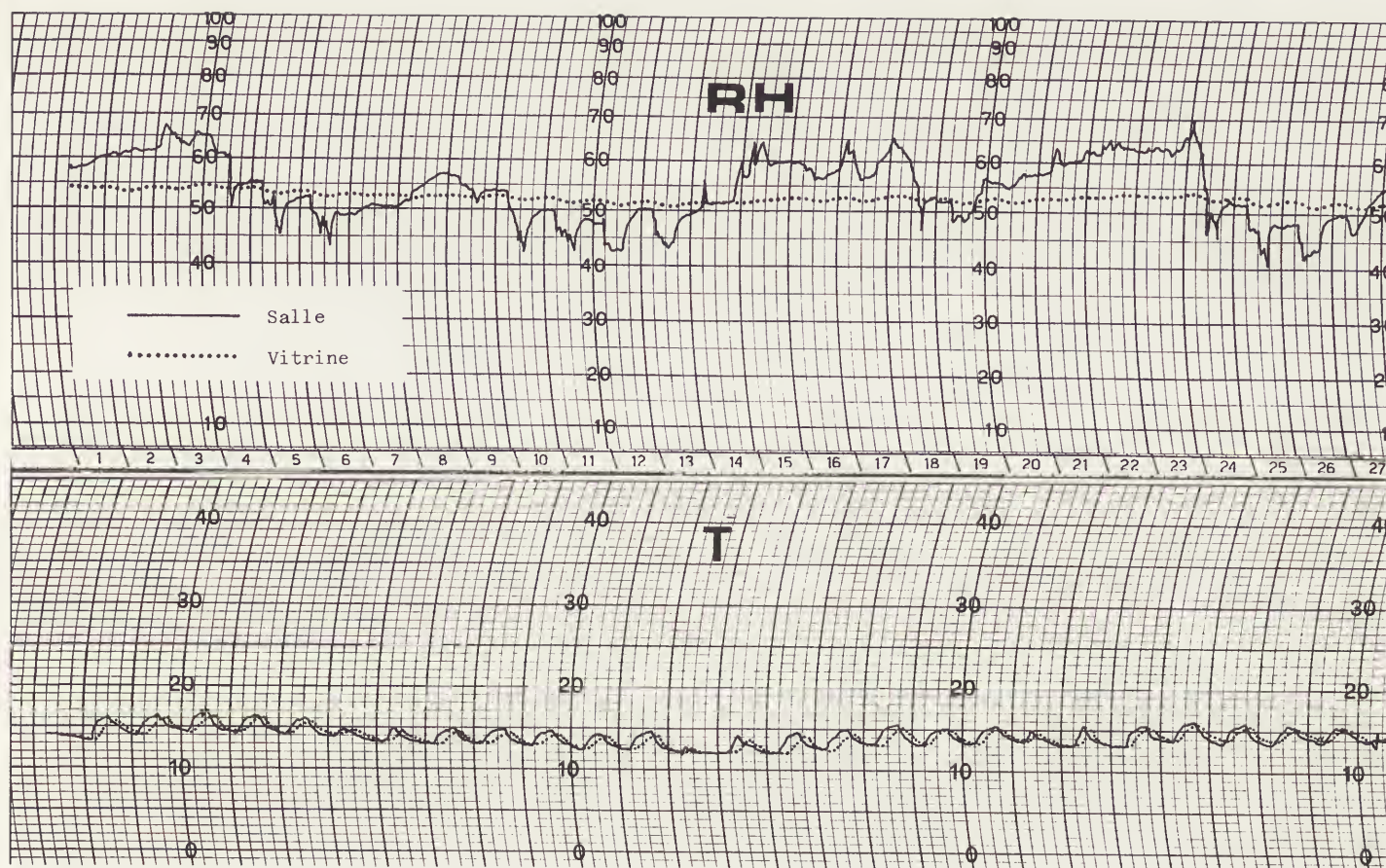
Fig. 8   Variations des conditions climatiques durant janvier 1984 dans la salle du
Palazzo Vecchio et dans la vitrine témoin.

de silice fut supprimé du double fond d'une vitrine comportant des instruments à vent donc peu sensibles aux variations hygrométriques. Durant ce mois les fenêtres ont été maintenues fermées et les variations d'humidité relative atteignèrent 15% seulement à l'extrieur de la vitrine. Mais ces variations furent quasiment intégralement répercutées à l'intérieur de la vitrine.

Ceci confirma le rôle du gel de silice dans la stabilisation de l'humidité relative dans les vitrines.

Afin d'améliorer encore les résultats obtenus, on a cherché à mettre plus en contact le gel de silice et l'air de la vitrine. Pour ce faire les trous de 5 mm de diamètre du double fond furent portés à 15 mm. Ceci n'apporta aucune amélioration appréciable.

Contrôles faits sur les violons

Avant d'être mis dans les vitrines les violons avaient été accordés à une quinte sous le diapason de la 440 Herz à 20°C.

A la fin des dix mois d'exposition on n'a observé aucun dommage. Aucune corde ne s'était détendue et aucun chevalet n'était tombé. De plus les violons étaient toujours au même accord. De plus, les violons n'avaient pas varié au poids (8) et ne s'étaient pas recouverts de poussière.

Après l'exposition

A la fin de l'exposition il était prévu de rapporter les instruments dans les réserves du Conservatoire Luigi Cherubini. Mais devant l'intérêt que cette collection avait soulevé dans le public il fut décidé de l'exposer d'une manière permanente au Palazzo Vecchio où elle se trouve depuis

maintenant trois ans. Le contrôle de l'humidité relative se fait toujours au moyen de gel de silice, l'enregistrement continu au moyen de thermohygrographe et les feuilles d'enregistrement indiquent que depuis trois ans l'humidité relative a varié entre 51% et 56% ne dépassant jamais 1% journalier (fig. 8). Il est important de noter que jamais il n'a été nécessaire de changer ou d'ajouter de gel de silice et qu'il n'y a donc aucune manipulation.

Conclusions

Les mesures faites au cours des quatre dernières années indiquent que l'humidité relative autour des collections est particulièrement stable. Ceci a pu être obtenu car l'humidité relative moyenne dans les différents lieux d'exposition correspondaient à celles requises par les collections. La stabilité de l'humidité relative à l'intérieur des vitrines a pu être obtenu en soignant particulièrement l'étanchéité des vitrines et en y ajoutant du matériel tampon préalablement équilibré à l'humidité relative voulu et en quantité suffisante.

Ces trois conditions ayant été réunies, cette méthode de stabilisation de l'humidité relative s'est revélée particulièrement satisfaisante et peu onéreuse.

Remerciements

Notes

1) <u>Preservation and Restoration of Musical Instruments - Provisional Recommendations</u>, A. Berner - J.H. van de Meer and G. Thibault - with the collaboration of N. Brommelle. London, Evelyn, Adams et Mackay, 1967

2) <u>Die Kunst des Geigenbaues</u>, O. Möckel - F. Winckel. Voigt-Verlag Handwerk und Technik, Hamburg 1967.

3) "Restoration and Conservation of Historical Musical Instruments" in <u>Making Musical Instruments, Strings and Keyboards</u>, London, Faber and Faber, 1979, p. 160.

4) Le change lire-U.S dollar était à cette époque de 1$ = Lit. 900

5) "Stabilization of R.H. in exhibition cases: hygrometric half-time", Garry Thomson, in <u>Studies in Conservation</u>, 1977, p. 85-102.

6) L'étude fut menée par P. Desideri, E, Ferroni, V. Gai, G. de Guichen et L. Morgantini.

7) Voir A. Bergonzi, "Il trasporto degli strumenti musicale" in <u>Cremona</u>, N. 1, 1980, p. 41.

8) Le poids d'un violon est naturellement fonction de l'humidité relative de l'air qui l'entoure. A titre d'exemple, voici les variations de poids enregistrées sur un violon non vernis et un violon vernis - non exposés - durant la journée du 26-9-83 durant laquelle l'humidité relative est passée à Florence de 82% à 20%.

Heure	Poids violon vernis	Poids violon non-vernis
	406,80	358,10
10h	404,40	354,36
11h		353,80
17h	402,50	351,70

Voir à ce propos l'article de V. Gai dans <u>Legno nel restauro e restauro nel legno</u>, 2e vol.

COMPARISON OF A MANUAL ENVIRONMENTAL MONITORING SYSTEM WITH A COMPUTER-BASED SYSTEM

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SUMMARY

A comparison of a manual environmental monitoring system and a computer-based system is made. Details are given of the problems associated with the manual system and how they are overcome with the use of a micro-computer and associated hardware. In particular the sensors and the interface unit are described. The capabilities of the software are given and the future expansion of the system is looked at.

In order to lessen the work load for environmental monitoring in a large museum some form of automated data collection and automated data analysis is necessary. Computers with associated hardware are excellent at gathering, storing, display and analysis of data. Computers don't get tired. They don't get bored. And they don't get sick.

The minimum conditions to be satisfied with environmental monitoring are the following:
*Storage and display of relative humidity and temperature values, over a period of time, of areas that we wish to monitor.
*Ability to store the data in an easily retrievable form.
*A summary of relative humidity and temperature data (weekly, monthly, and yearly) so that sensible and usable conclusions about the environment can be reached.
Such a computer-based system has been installed in the Australian Museum and has been operating now for over twelve months on a routine basis. It is with this experience that a comparison of its work effectiveness can be made with a manual monitoring method.

Manual Monitoring Method

In order to achieve the above conditions the following manual monitoring method was carried out. Nine areas were monitored and all contained humidity sensitive ethnographic objects. The areas were of two types: 1) relative humidity and temperature controlled i.e. airconditioned; and 2) uncontrolled areas.

The equipment used for monitoring these areas consisted of thermohygrographs and a sling psychrometer. The method, briefly involved placing a thermohygrograph in each area to be monitored. Each week the used charts are collected and replaced and the calibration of the thermohygrographs is checked with a sling psychrometer. Once the charts are collected the trace is analyzed in order to provide the following information. The minimum and maximum relative humidity and temperature, is noted. The relative humidity trace is divided into 5%RH bands and the time spent in each band over the week is recorded. The mode is the 5%RH band in which the greatest

amount of time was spent e.g. it may be 45-49% RH. We also have desirable limits for the relative humidity of 50-60% and the time spent outside these limits is recorded.

So in summary, our manual monitoring system involved the calculation of: minimum and maximum relative humidities and temperatures, the modal 5%RH band and the time spent outside our limits of 50-60% for each week.

The labour necessary to do all the above for monitoring the nine areas, was about 1.5 days per week.

Problems Associated with the Manual Monitoring Method

There are three problems associated with the described manual system.

Firstly, it is usually very difficult to increase the number of areas being monitored because of the time/labour committment. Secondly, in order to try more statistical treatment of raw data (and that means gaining more significant trends), yet more time/labour is needed.

Lastly, there is a problem with the accuracy of the readings because of the limitations of the equipment. Thermohygrographs have an accuracy of 3% at best and typically $\pm 5\%$. In fact it is difficult if not impossible, to find a rugged, reliable and accurate relative humidity recording device.

If we wish to know our environment well in order to minimize the damage caused by it then we need to have confidence in the relative humidity readings. Accuracy in the measurement of relative humidity is a problem for the following reasons:
i) desirable limits are set at 50-60%RH. These boundaries are strict and it is necessary to know if the relative humidity is definitely in the range or not.
ii) to find the modal 5%RH band requires an accuracy of 2% or better.
iii) the method for calibrating thermohygrographs to ensure their stated accuracy over a range of relative humidities is difficult to set up because of the size of thermohygrographs, i.e. it is very complicated to maintain a range of relative humidity environments which are stable, accurately known and large enough to allow access for thermohygrographs.
iv) the slow speed at which the hair reacts can give misleading results when the relative humidity is changing quickly. In controlled environments it can sometimes vary widely in a short period of time. For example, results from some thermohygrographs have shown only a deviation of $\pm 10\%$ whereas in the same area, other measuring methods have shown one of $\pm 20\%$.

Computer Applications

There are two ways of making the use of computers efficient for environmental monitoring.

Firstly, a data logger collects and stores the data. After one week of results has been recorded the data in the logger is fed into a computer and the computer then calculates what it has been programmed to do e.g. the temperature range, the mode etc. The data logger's memory is erased and then it starts gathering data for the next week. For further description of this system see Thomson, 1981.

The second way of using a computer for this purpose is to let the computer collect, store and analyse the data as it is being received. The computer is its own logger. This is called a dedicated on-line computer and is

able to simultaneously collect the data and analyse it.

It was decided that the second alternative would be better for two reasons: price and versatility.

With a dedicated micro-computer system it is possible to display and store current relative humidity and temperature readings, calculate the mode and graph the results each time a new value is received. It is possible to carry out further functions such as alarms to warn of potential disasters, control relative humidities in enclosed environments, carry out more data analysis and so on. Its versatility is almost unlimited.

Minimum Design Criteria for Computerised Monitoring System in Museums

The equipment should satisfy the following criteria: Relative humidity accuracy no greater than ±1% over the range 30-90%RH. Temperature accuracy of ±0.25C. Ability to monitor at least ten seperate areas (up to 400m away from computer) at once. Ability to permanently store the data in an easily retrievable form. Rugged, reliable and accurate sensors. Within a modest budget (in our case $U.S.9,000).

In fact, despite extensive investigations, we found no system, at any price, which met the above criteria.

Therefore, a computerised system had to be designed and built for us, to meet the above criteria.

The Computerised System

The complete system has met all our design criteria and in some cases exceeded them.

Hardware

The hardware consists of the following: a micro-computer (Commodore "Pet"), a disk drive, a graphic printer, an interface unit and sensors.

The disk drive is used for long-term storage of the environmental data (relative humidity and temperature readings, and the time of the readings) over a one week period. The dot matrix printer (Epsom MX80 type III), for the majority of the time, acts as a multichannel chart recorder plotting the relative and temperature values over the week and, at the end of the week, printing the summary of the data.

The micro-computer, disk drive and dot matrix printer are readily available and there are many from which to choose. However, what makes our system unique is that a suitable interface unit and the sensors were specially designed to meet our specifications. It is these two parts of the system that need further explanation.

Interface Unit

The interface unit is capable of having up to 128 sensors measuring relative humidity and temperature connected to it. Under instructions from the computer, the interface unit collects relative humidity and temperature data from each sensor and transmits that data to the computer. The power supply for the sensors is also incorporated in the interface unit. This unit, as well, is designed to receive data other than relative humidity and temperature if the data is transmitted in a similar form. For example it would be possible to also monitor light levels, pollution levels, etc.

Relative Humidity and Temperature Sensors

The accuracy of the computerised system depends almost totally on the hardware designed to measure relative humidity. Tempteratue is relatively easy to measure accurately. However the accurate measurement of relative humidity is difficult.

The sensors are reliable, rugged, accurate and quite small (155x65x30mm). Installation is quite simple because only one wire carries the relative humidity and temperature information as well as the power required for it to operate.

After five months of constant use the sensors were found to be still calibrated to within our specifications (i.e. ±1%RH and ±0.25C) and so making the need for calibration checks infrequent.

The relative humidity sensing element that offers the greatest stability (and hence accuracy) with regard to the museum environment is the one which changes its capacitance with a change in relative humidity. The response of the capacitance sensor to relative humidity, in the long term, should be more stable than other electronic sensors which change their resistance or impedance with changes in relative humidity.

There are two types of relative humidity sensing elements of the capacitance type which are readily available. One is made by Vaisala and the other by Philips. The Vaisala element has a faster response to a change in relative humidity, however it is expensive. The Philips sensor is fast enough for continual environmental monitoring at a much lower price.

Calibration of the Sensors

In order to test the calibration of the sensors, a method was refined which allows accurate relative humidity standards to be compared with the sensors measured humidity values. The standards are based on the principle that some salts in a saturated solution will, under certain conditions, maintain an equilibrium relative humidity above the solution. This calibration system is awkward to maintain but does, with care, have an accuracy of ±0.2% or better.

Software

No software was supplied with our equipment. The software is the "programme" or set of ordered instructions that the computer carries out. The software was developed by the author. A programme had to be developed which would at least do all that the manual monitoring method was achieving.

The following capabilities were soon realized. Data is collected from each sensor every ten minutes. Then the raw data is converted into a %RH and Celsius. This data is then statistically analysed, plotted on the dot matrix printer, displayed on the monitor and stored on floppy-disk. After one week of the above, the computer calculates the maximum and minimum relative humidities and temperatures, the mode, mean and standard deviation for the relative humidity record over the week, the % of time spent outside 50-60%RH desirable limits and a frequency versus 5%RH band table for each sensor for the week.

One important aspect about the software is the time and specialized labour required to develop it for a specific purpose. A considerable amount of time (a few months in total) has been spent developing the programme. It

is now at a stage where it can be used for
routine monitoring purposes and, also, as a
research tool for environmental monitoring.
The software is in Basic-4 computer language
and is available for use by other Museums
using a similar system. We hope that this
will lead to further development and refine-
ment of the software at little or no cost to
the users.

Future Use

The computer system now calculates all that
the manual method was achieving, but it also
establishes the mean and standard deviation
for the relative humidity record for each
sensor for the one week period.

Anticipated routine use includes alarms
written into the software to minimize any
damage caused by a disaster (such as malfunct-
ioning or water leaks), and also expanding
the number of areas to be monitored.

For research purposes, the following will be
examined:
New applications of numerical analysis will be
developed in order to find more significant
environmental trends with regard to damage to
museum objects.

Other damaging environmental factors will also
be monitored, such as light or pollution.

The response of wood in a museum object to a
change in relative humidity will be investig-
ated.

Conclusion

In conclusion, a computer-based environmental
monitoring system has many advantages over a
manual system. Firstly, it will save
considerable time and labour. It is accurate.
It will easily allow the expansion of the
number of areas being monitored and in the way
in which the weekly data is summarized.

The centralized display of the readings on
the computer monitor makes it easy for the
Conservation Department at the Australian
Museum to determine the relative humidity and
temperature conditions around the Museum, at
that time. Also, the computerized humidity
and temperature record is in a more convenient
form for futher analysis. On the other hand,
the record from the manual method is in a
very tedious form, requiring a large labour
input.

There are initial drawbacks with the computer
system, such as installation and familiar-
ization with the equipment. However the
investment in such a system is worthwhile, if
only for the improved interpretation of the
relative and temperature record and the labour
saved.

The specialized equipment (i.e. the interface
unit and sensors) used in our system is
readily available from the manufacturer*and
it is only through his help and patience that
this system was designed and built to our
specifications, at a most competitive rate.

*Mr R. Fisher, Technequip Enterprises, Austra-
 lia.
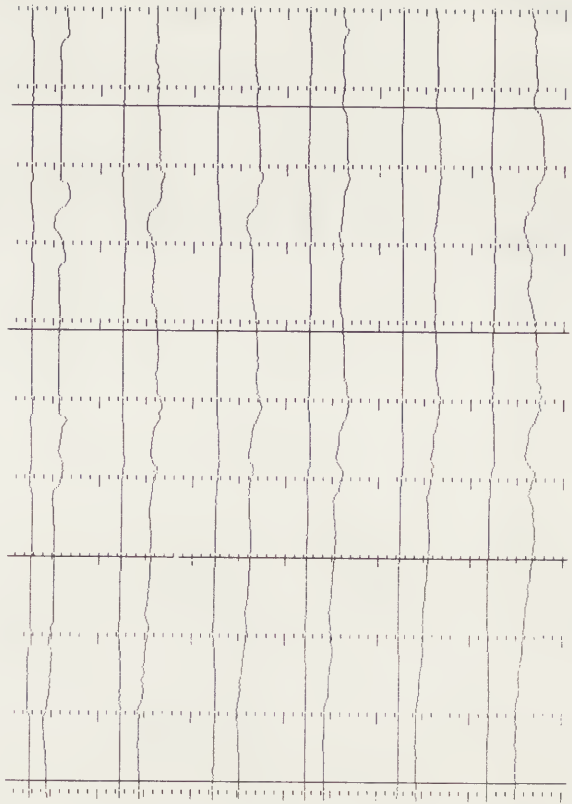
Fig.1 Section of printout of graph of relative
humidities and temperatures plotted on a dot-
matrix printer. Information from six sensors
is shown in six pairs (i.e. one temp. and one
RH record in each pair). Scale, for the six
consecutive channels, is 0-100 for each
channel. Unbroken horizontal line occurs at
mignight of each day.

Fig.2 Weekly summary of relative humidity and
temperature records, prepared automatically at
the end of each week.

Reference

Thomson, Gary, "Control of the Environment for
Good or Ill? Monitoring", Nat. Gall. Tech.
Bull., 3, 1981, pp. 3.

TABLE DISPLAY CASE, NATIONAL MUSEUM OF IRELAND

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SUMMARY

This paper is a short description of the design of a
table case for the National Museum. It is primarily
concerned with the technical aspects of the design.
The case was made for a specific exhibition. Due to
time restrictions it was not possible to make
prototypes with the result that certain minor
difficulties and faults remain to be corrected.
However, in use the case has been reasonably successful
and the design is capable, with small modification, of
satisfying all the relevant climatic and conservation
criteria.

INTRODUCTION

This table was designed in 1982 for a special
temporary exhibition to celebrate the centenary of the
birth of Eamonn de Valera, the Irish Politician and
Statesman. It was subsequently re-used, with some
modification, for an exhibition to celebrate the
anniversary of the founding of Grattans Parliament.
In both instances the cases were to contain
manuscripts and papers with very specific conservation
requirements.

The exhibitions of which these cases wher part took
place in the rooms of the 19th Century National Museum
building in Dublin. It was initially decided by me
that the Architectural strategy for the exhibition
design should be to emphasise the existing character
of the rooms rather than make a particular installation
for the exhibition. The rooms are basically square in
plan with vaulted ceilings, mosaic floors, casement
windows and highly ornamental ceramic door surrounds
and fireplaces.

In short, the rooms had a distinctly 'Roman' character
and I decided to emphasise these aspects in my design.
The decorative scheme chosen was pompeiian in feeling
with etruscan red walls and raw umber ceilings. All
the pieces of furniture, including the radiator covers,
display cases and light fittings were designed by me in
a style which I felt to be appropriate to the setting.

The table case which is the principal item of furniture
in both exhibitions is consequently sober in character
and uses the traditional museum type with modifications
to satisfy the technical requirements of modern museum
conservation.

REQUIREMENTS

These technical requirements were very detailed and may
be classified under the various headings of lighting,
humidity, security and dust control. The lighting
requirements consisted of keeping a constant light level
at a figure below 50 lux and the elimination of ultra-
violet radiation. For the safety of the documents it
was necessary to maintain constant levels of relative
humidity within the cases. The requirements from a
security point of view consisted primarily of the
prevention of forcible entry or damage to the cases.
Finally, dust seals were required to prevent
deterioration of the documents through ingress of dust
into the cases, particularly as the rooms are naturally
ventilated with the attendant problems of atmospheric
pollution.

VENTILATION SLOTS

REMOVEABLE 'ROOF'

LIGHT BOX

DOCUMENTS

SILICA - GEL

POWER SUPPLY
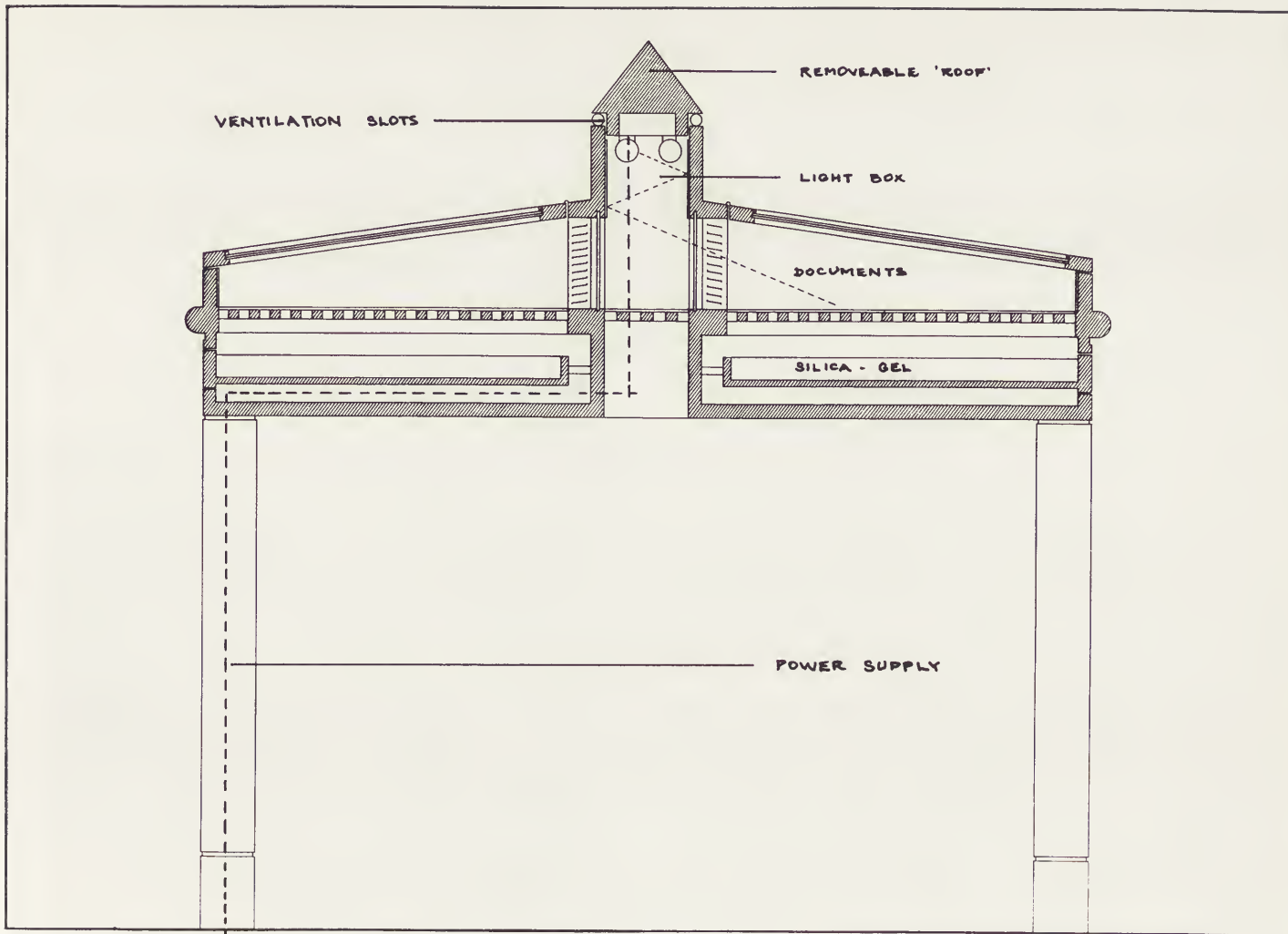
DESIGN

The design of the case consists basically of a table
supporting two back-to-back cabinets separated by a
raised light box to illuminate the documents. It has
eight legs which are grouped in pairs of four and
strengthened by diagonal corss-bracing. The cabinet
measures 8'0" x 4'0" x 5'0" tall and it is constructed
if mahogany with a black lacquered finish. The metal
beads, tie bars and ironmongery are all of polished
brass.

The detailed cross section illustrates the principal
features of the design: the raised light box; the
various filters; the document cabinet and the secret
drawer below containing silica-gel.

LIGHTING

The removable 'roof' of the case contains the lighting
mechanism which consists of two 40 W flourescent
tubes with built in ultra-violet filters. Originally
this section also contained the starting gear for
these lights but in use it was found that this
feature lead to considerable overheating and these have
subsequently been removed and mounted remotely for
safety.

The power supply to the lights comes from under the
floor through one of the hollow legs, to the light box.
The ventilation of this section in the original design
was also found to be inadequate and this has now been
modified as shown on the cross section: The base of
the case is now slatted and there is a continuous
ventilation slot below the 'roof'. The small brass

spheres act as spacers and this revision has been found
to be quite satisfactory.

The walls of the section directly below the light
fitting are lined with mirrors for two reasons:
Firstly, so that the actual fittings are concealed from
view in order to eliminate glare and, secondly: to
ensure that the light falling onto the documents is
evenly spread across the width of the case. There is
one further mirror on the side of the case opposite the
light source which reflects light back and this also
helps to maintain a uniform light level within the
cabinet.

FILTERS

Between the light box and the document cabinet there
are three layers as follows: an ultra-violet filter; a
set of louvres and a sheet of non reflective glass.

It was felt that an ultra-violet filter was required at
this point as the danger existed that at some time the
original flourescent tubes might not be replaced with
fittings of the appropriate type which would lead to
damage to the documents. It is not essential but I
felt it desireable that this filter be included.

The louvred screen was installed principally to
eliminate glare and prevent a clear line of vision from
one case tp another. The louvres as fitted are made of
timber but in subsequent tests I have found metal to be
more satisfactory on account of their lighter section.
The louvres are not all at a constant angle but each may

VENTILATION

REFLECTIVE MIRROR LININGS

2 NO. 40 WATT FLOURESCENT TUBES

ULTRA-VIOLET FILTER

TYPICAL LIGHT PATH

ADJUSTABLE METAL LOUVERS
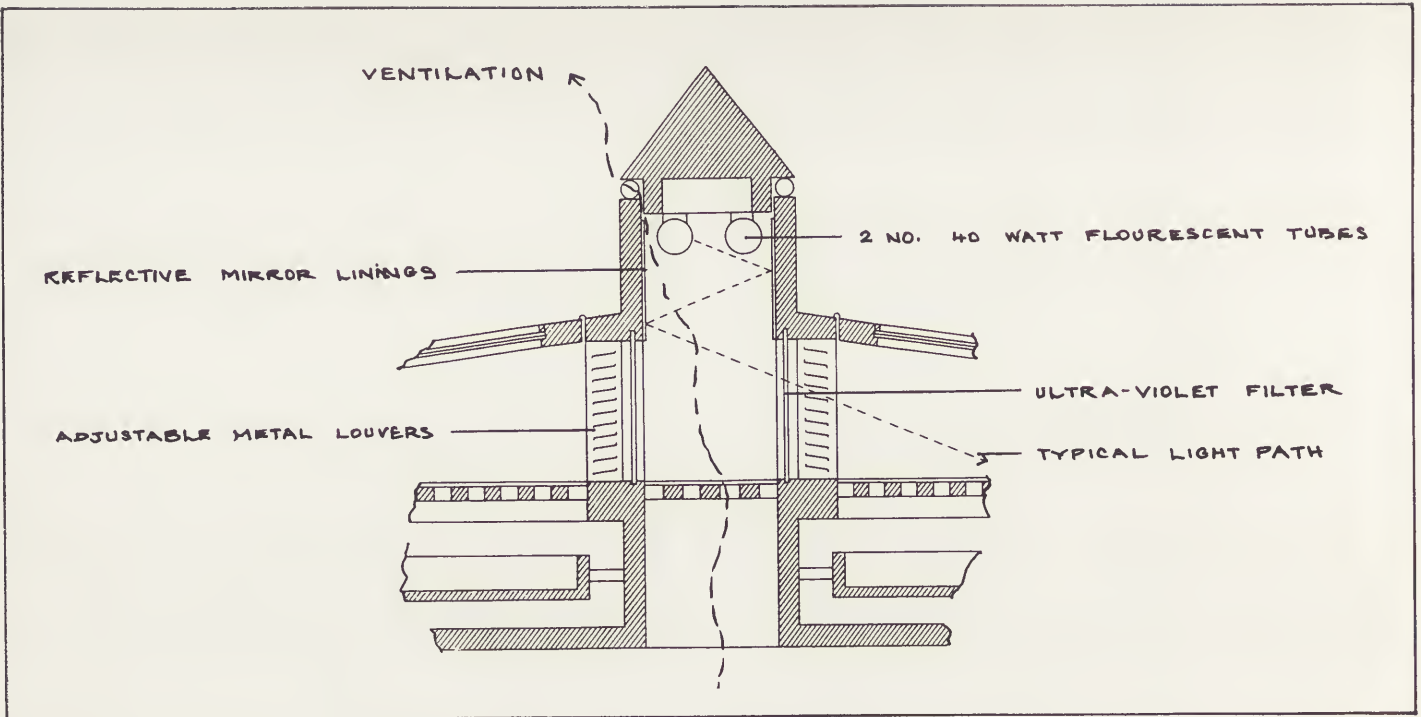
be adjusted to control the spread of light over the documents. It was found that even minor adjustments can result in significant amounts of shadow being cast on the documents within the case. The final element of this build up, the non-reflective glass, is used simply to mask the existance of the louvres. The result is reasonably successful, the effect being of a black screen behind the glass.

DISPLAY COMPARTMENTS

The section containing the manuscripts consists in fact of two cabinets; one containing the actual objects and a second containing pre-conditioned silica-gel.

The upper cabinets contain the manuscripts which are individually mounted and displayed in an appropriate manner. This case has a laminated glass top which is hinged in a wooden frame. The glass used is the laminated anti-bandit type which provides security against attack and ultra-violet penetration. The wooden frame is rebated on all sides and sealed to maintain constant levels of relative humidity within the case and also to prevent the entry of dust, etc. into the case.

The base of the upper cabinet is constructed of slatted timber to allow free circulation of air from the compartment below containing the pre-conditioned silica-gel. This sealed drawer is lined with polythene to prevent absorption by the surrounding wooden construction.

DUST SEALS

LAMINATED GLASS TOP

MANUSCRIPT

SEAL

MIRROR

DRAWER WITH PRE-CONDITIONED SILICA GEL

84.17.31
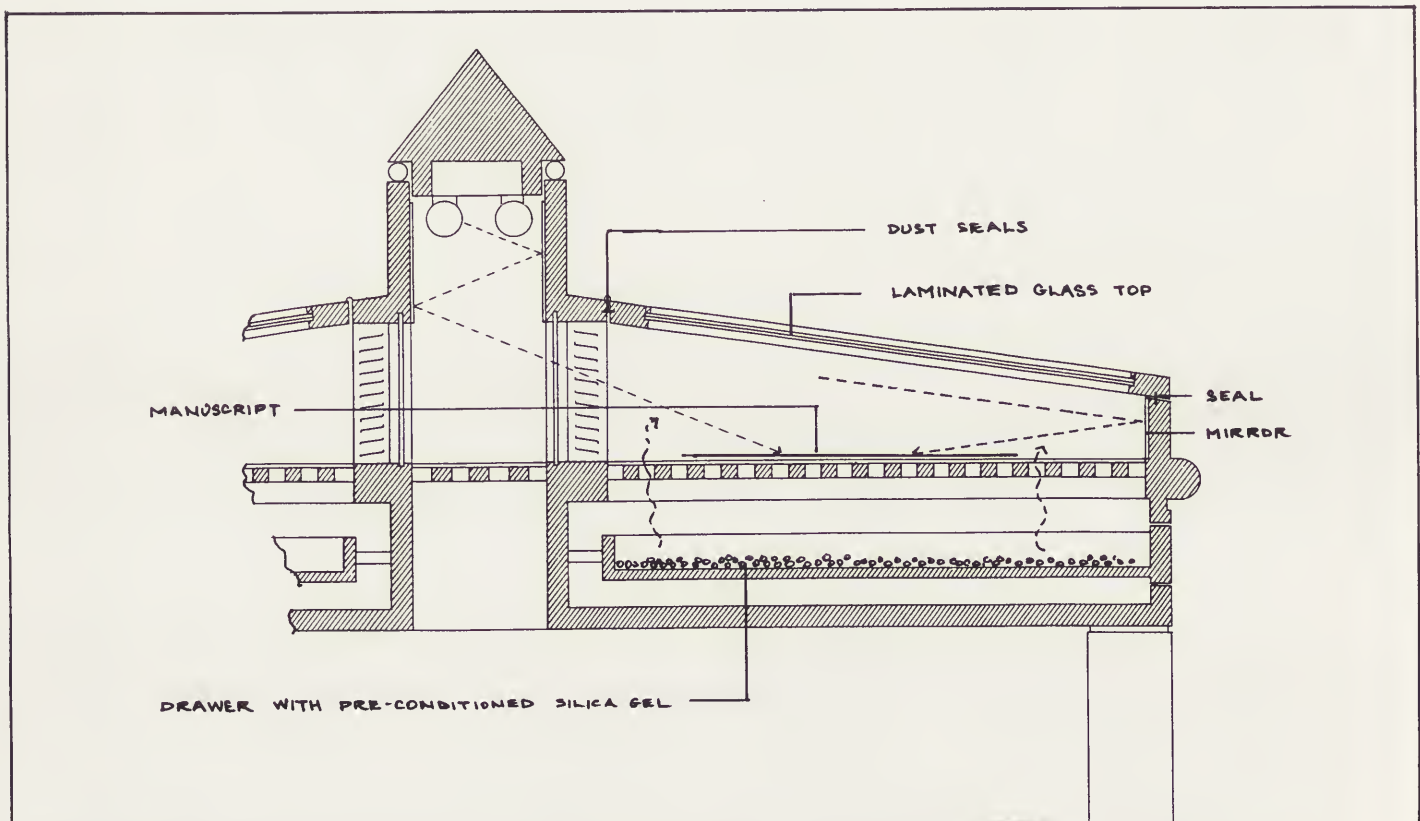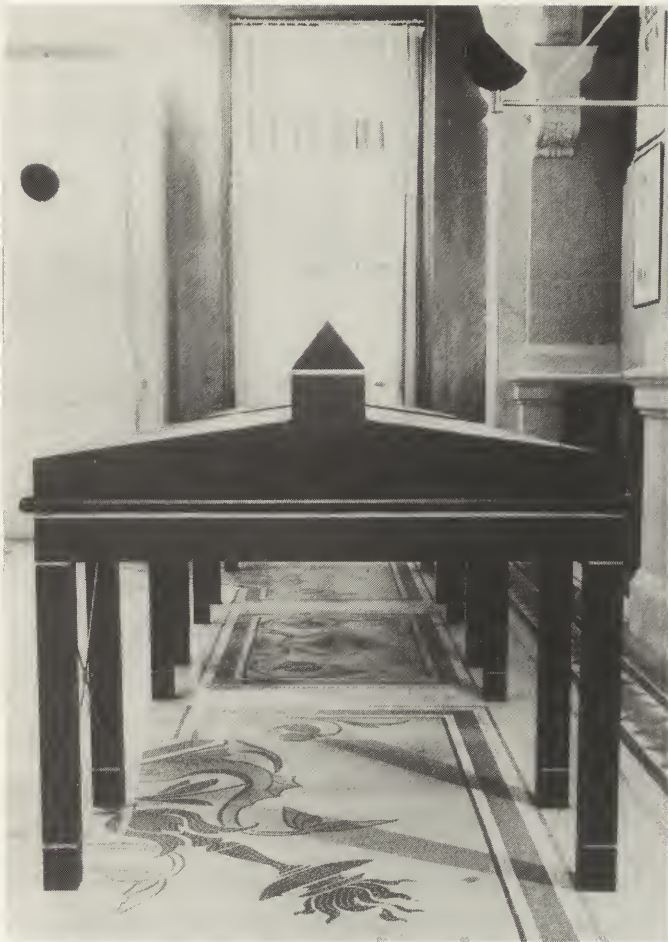
Access to these two individual areas is kept separate for conservation and security reasons: To change the silica-gel it is necessary only to open the lower compartment, whereas access to the upper section which is restricted and less frequent, is controlled by the curator.

and no special components were used in their construction. In the general design of the fittings it would seem that the adherence to a set of established and well recognised principles will provide adequate climatic control without inhibiting the aesthetic intentions of the designer in any way.

CONCLUSION

These cases which have now been in use for eighteen months were made by traditional furniture manufacturers'

Fundamentally, what has been attempted here is the use of a traditional and familiar type which is modified to suit its location and to incorporate the technical requirements of modern museum conservation.
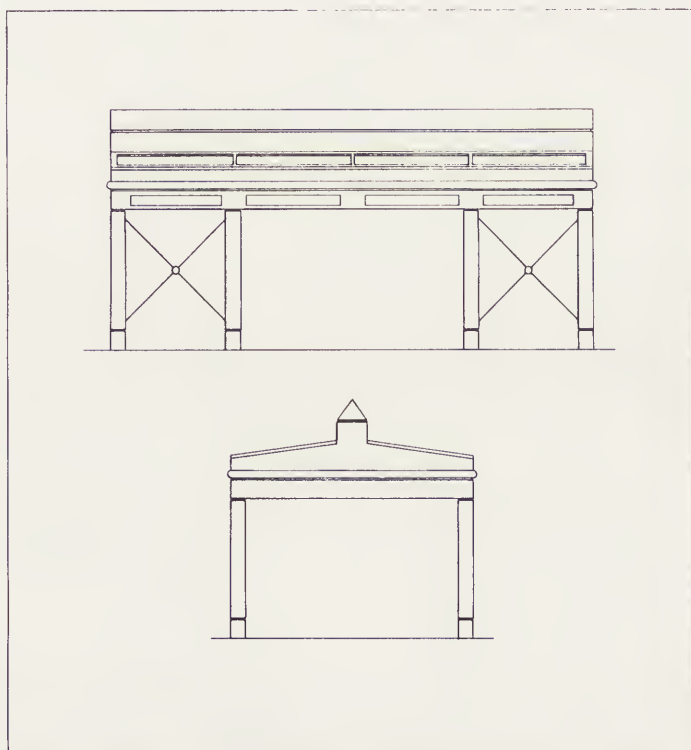
THE CONTROL OF RELATIVE HUMIDITY – RECENT DEVELOPMENTS

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Abstract

Recent developments at the Canadian Conservation Institute (CCI) in the area of relative humidity (RH) control are discussed. This includes two novel methods of RH control for museums, art galleries and historic houses: humidistatic controlled heating and a relative humidity control module for display cases. The operation and performance of each system is explained and results of field trials are presented. The issue of air leakage in display cases is discussed with emphasis on the factors determining the "leakiness" of a case.

Introduction

Adverse relative humidity conditions and fluctuations can cause irreversible damage to artifacts and works of art. Consequently, museums and art galleries have strived to maintain stable RH conditions in their display and storage areas. Various methods of control have been utilized ranging from the simple and cheap portable humidifiers and/or dehumidifiers to the sophisticated and exorbitantly expensive climate control system for whole buildings. Self-contained systems often used in computer rooms have also proved to be successful, particularly in selected spaces rather than complete buildings. Three installations have been recently installed in Ottawa at the recommendation of the Canadian Conservation Institute. The use of sealed and buffered display cases is another approach which offers very good control of humidity.

Most of these methods, if not all, have certain drawbacks and limitations. Some are too expensive, others provide only limited control. As well, any solution in which the complete building (or rooms with exterior walls) is humidity controlled during the cold season, can potentially lead to serious structural problems. Moisture diffusion and movement through walls and seams during the cold winter months can irreversibly damage the wall fabric, if the latter was not properly designed and constructed. Excess moisture can promote rot and corrosion of structural materials inside the walls. This has led to some relaxation of RH standards for Canadian institutions[1]. Also, it has forced people to consider options in which localized RH control is provided such as buffered display cases and the "room within a room" or "cocoon" approach.

The search for and development of new methods of RH control goes on constantly. At the CCI, the Environment and Deterioration Research laboratory is often called upon to advise on environmental problems in Canadian museums and art galleries. This continuous exposure to environmental issues has led to the development of novel solutions and ideas at the Institute. Two particularly important developments are described in this paper: Humidistatic Controlled Heating and A Relative Humidity Control Module for Display Cases. The issue of display case air leakage is also discussed.

Humidistatic Controlled Heating

The method referred to here as humidistatic controlled heating is a novel approach to humidity control.[2] However, the concept on which it is based is certainly not new. Rosenberg suggested in 1933 that high summer RH could be lowered by increasing the ambient temperature a few degrees[3]. A similar approach was developed in England but few tests have been carried out[4,5]. The tests described in this paper are, to the authors' knowledge, the first attempt at utilizing the method in Canada. The fundamental principle on which the technique is based can be stated as follows: the relative humidity of a given volume of air at a constant absolute humidity (moisture content) will decrease when its temperature rises and conversely, the RH will increase if its temperature is allowed to cool. The corollary of this statement is that if the absolute humidity of a volume of air changes constantly, it is possible to maintain a stable RH by continously varying the temperature of the air. Humidistatic controlled heating does exactly that – it varies temperature to maintain a stable RH.

In its simplest form, the method consists of replacing the thermostat of the heating system with a humidistat. Thus, the temperature of the building is no longer dictated by heating demand but instead by whether the relative humidity is too low or too high. If the interior RH is above the set-point of the humidistat, the heating system will be switched on. Ambient temperature will increase causing the RH to decrease. Once the humidity reaches the set-point, the heating system is switched off.

In this basic form, the system could potentially lead to excessively high or low temperatures. The addition of two cut-off thermostats completes the system. One thermostat serves as a high limit cut-off and is normally set at about 22°C. The other serves as a low limit cut-off. Its setting determines to a great extent the performance of the system and will be discussed later. Figure 1 shows a typical wiring diagram.

TO FURNACE RELAY

T-1

H-1   T-2

T-1 LOW LIMIT THERMOSTAT
T-2 HIGH LIMIT THERMOSTAT
H-1 HUMIDISTAT (HUMIDITY CONTROLLER)
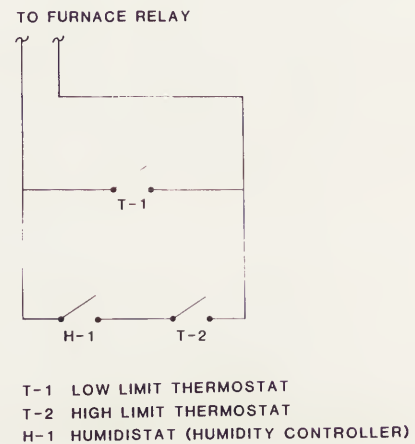
Figure 1 Wiring diagram for the humidistatic controlled heating system.

The operation of humidistatic controlled heating is best explained by examining the results as shown by selected hygrothermograph charts. The results shown in Figure 2 were obtained during the first winter of testing in a historic house at the Kings Landing Historical Settlement in New Brunswick, Canada. The following sequence of events can be shown to have occurred over a 15 day period. (RH set-point = 50%; low limit = 10°C; high limit = 22°C).
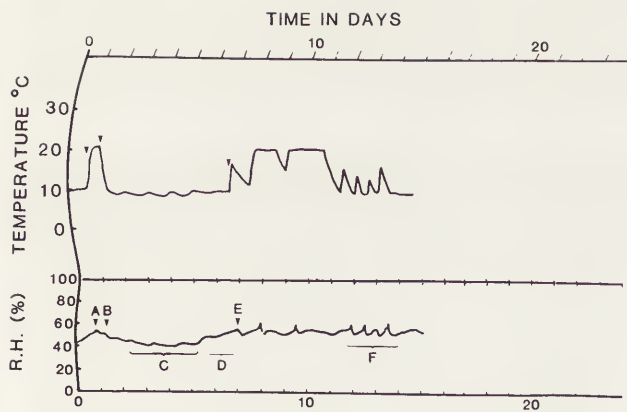
Figure 2 Hygrothermograph chart showing the changes in temperature and relative humidity in a building with humidistatic controlled heating.

A. RH increases until at point A the heating system is switched on. Temperature increases causing RH to decrease. Temperature reaches the high limit value and remains there;

B. at point B, RH begins to decrease and the heating system is shut-off. Temperature decreases until it reaches the low limit setting;

C. RH remains below set-point and is uncontrolled since temperature cannot decrease further. A lower setting on the low limit cut-off thermostat would have allowed temperature to decrease further and RH to increase and reach the RH set-point.

D. RH begins to rise because of an increase in absolute humidity; at point E, the humidistat's set-point is reached and the heating system is switched on;

E. temperature rises and RH drops to 50%;

F. a typical control sequence is shown.

During the first trials, an inexpensive nylon ribbon humidistat was used. It had a relatively slow response and high differential. This led to an RH control of no better than ±5% when temperature was between the two cut-off limits. For the second winter of testing, a more accurate and sensitive humidistat was installed. This provided a much improved control of RH as shown in Figure 3.

Figure 3 Same as Figure 2, but for a different time period and with a more accurate humidistat installed as RH controller.

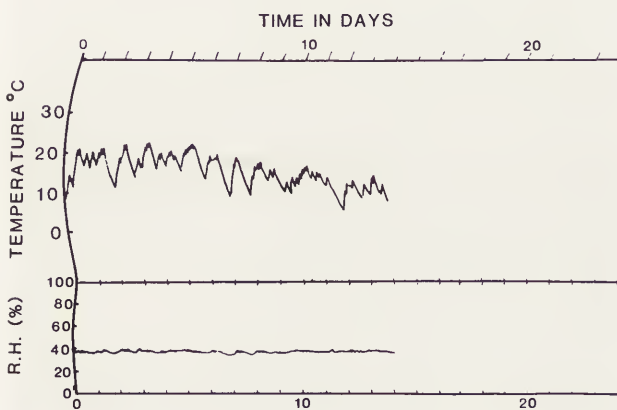The importance of the low limit thermostat setting has been mentioned earlier. In very cold areas, the exterior absolute humidity is so low that even a slight heating to 5°C inside a building is sufficient to lower the relative humidity to unacceptably low levels. A reduction of the low limit temperature setting wil allow the maintenance of an acceptable level of RH. Figure 4 shows the results of disconnecting the low limit thermostat completely. Prior to the disconnection, the low limit had been reached and the RH drifted uncontrolled. Without the cut-off thermostat, temperature was allowed to decrease until RH increased sufficiently and the humidistat again took control of the heating system.
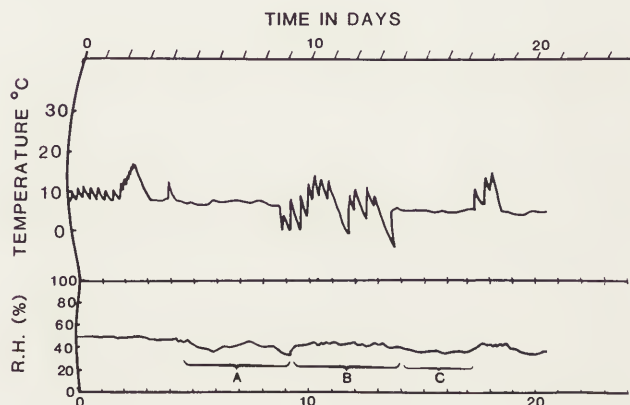
Figure 4 Same as Figure 2, but for a different time period. In region A and C, the low-limit thermostat set-point has been reached and RH is uncontrolled. In region B, the low-limit thermostat has been disconnected causing RH to increase and be controlled by temperature variation.

It is recommended that the humidistat be set within the range of 35% to 50%. In cold areas, the set-point should be at the lower end of this range while for areas with milder winters, the upper end of the range would be suitable.

As was mentioned earlier, this system is not without limitations. It is not suitable for all institutions. The following list identifies the prerequisites and drawbacks of this procedure:

1. It only deals with the RH problem during the cold season (usually late fall, winter and early spring).

2. The building must have a heating system which is easily controlled by electrical switching.

3. The system works best in buildings that are insulated and well sealed.

4. The building should have good air circulation.

5. The institution should be closed to the public or have limited occupancy; widely fluctuating temperatures would prove uncomfortable to the occupants.

The system is therefore applicable to the small or medium size museum that is closed during the winter season and also to storage buildings which have only limited occupancy.

The final question that must be answered before humidistatic controlled heating can be recommended is "how will widely fluctuating and relatively low temperatures affect the artifacts?" Thermal expansion and contraction are much less pronounced than the dimensional changes which result from variations in relative humidity. For example, it has been shown that for a 30°C change in temperature, ivory will undergo a 0.1% dimensional

change[6]. However, a 1% dimensional change will result when the relative humidity varies by 20%. Furthermore, the possibility of ice crystal formation inside materials is remote. Studies have shown that in materials with typical moisture contents (less than 15%), the absorbed water does not undergo any ice-like phase transition at 0°C or below, nor is there any significant change in the distribution of the water[7,8,9].

Humidistatic controlled heating has been in use at Kings Landing for four winters and no major problems have been reported. The authors are aware of at least two other institutions which have installed this system as a result of our developmental work. It is our intention to collate the results of these subsequent installations in order to identify potential problems.

Relative Humidity Control Module

Over fifty years ago, museums recognized explicitly that display cases offered RH stability if they were fairly airtight.[10] At the same time, patents appeared for additional "regulating substances in cases and picture frames."[11] In those days it was salt hydrates, later saturated salt solutions.[12] Over the last two decades, silica gel has dominated the buffer approach. The method is ideal if only a few cases are to be controlled but, in CCI's experience, there is a great deal of museum resistance to its application en masse. It is perceived as a labour intensive inconvenience.

In 1978, Raymond Lafontaine proposed the marriage of mechanical control system convenience with silica gel stability. A single module would pipe clean air of correct RH to all cases in a hall or gallery. The module would contain mechanical humidification and dehumidification components. Their output would pass through a silica gel buffer in the module. By 1981, the concept had been implemented in a prototype by Stefan Michalski. The internal design has been detailed elsewhere.[12] The following will discuss application of the module.

Museums have been traditionally opposed to the use of a central mechanical system to supply controlled air to display cases because this system would require large ductwork for distribution. The key to acceptance of piping was small size. In the CCI design, plastic tubing is used, not bulky ductwork. Module pressure (2 kPa) is higher than that of ordinary ventilation systems (0.1 kPa), although it is far below dangerous pressures encountered in "compressed" air applications (300 kPa). The module air "pump" is a centrifugal blower that is quiet and maintenance free. The tube diameter to each case depends on distance, case volume and leakiness. These pipe diameters (see Figure 5)
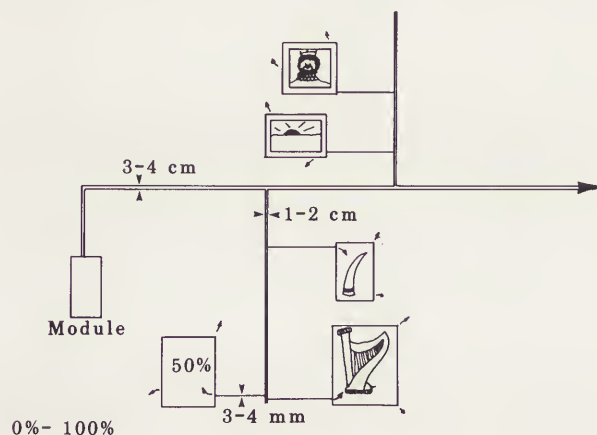
range from 2 mm for glazed pictures to 1 cm for cases of ten cubic meters. With a main supply pipe of 4 cm diameter, the module can be up to 50 metres away. The most appropriate piping in these size ranges is plastic plumbing or garden hose for the main net- work, and smaller transparent vinyl tubing to each case.

The most common question asked about the module has been "what is its capacity", or "how many cases can it control". The brief answer is between one and one thousand cases. The complete answer depends on two factors: case size and quality of construction. The latter is the most important. The better the quality and the fewer the number of cracks, the greater the number of cases which can be controlled.

Cracks in poorly sealed cases determine the transfer of air and moisture to and from the exterior. Rate of transfer can be measured as exchange rate, whether it is by diffusion or convection. For convection, the building industry expresses air leakage as air changes per hour.*

Thus a case of 2 m^3 that leaks in one side and out another at a rate of 4 m^3/day is said to leak at 2 acd (air changes per day). Very carefully sealed cases have approached moisture exchange rates of one per two days.[14] Such cases approach a diffusion controlled limit: moisture diffusion through a five sided polymethyl methacrylate[15] lid (6 mm thick) is equivalent to about one exchange per ten days. (1 m^3 case). Padfield emphasized simple diffusion of moisture through stagnant air in cracks: a 0.5mm crack along four sides of a 1 m^3 case allows moisture diffusion equivalent to one air change per two days. He also showed that pumping of the case due to diurnal temperature fluctuations or to barometric pressure changes was negligible: one air change in several months.

All that remains to explain the rapid moisture loss or gain of ordinary museum cases is convection, i.e. draughts. If a 1 m high case has a light box on top with a 0.5 mm crack in the seal all around the perimeter of the glazing (6 mm thick) and a similar crack exists around the base of the case, then a temperature difference or an RH difference between the room and the case leads to a chimney effect. For 2°C or 40% RH, the leakage is one air change per six hours. (The temperature differential may be due to heat from lights or simply thermal inertia of the case contents during diurnal room change.) A 1 mm gap raises leakage to one air change per hour. All these moisture transfer mechanisms are summarized in Figure 6 for a 1 m high case. At less than 0.1 mm crack width, diffusion through the PMMA sides dominates. Between 0.1 mm and 0.3 mm crack width, diffusion through stagnant air in the gap dominates. Above 0.3 mm, convection dominates and increases rapidly, since airflow through the gap is proportional to width to the third power. Convection does not arise if the cracks are all at the same level of the case. Also, the two pressure sources, temperature and RH differential, may cancel each other: high case temperature causes case air to rise, low case RH causes case air to sink. However, a temperature difference over 1°C will swamp RH differences.

With the above understanding, the module capacity can be clarified. The module generates 400 m^3/day of filtered and RH controlled air. Air should be supplied to each case at a rate at least double the natural leakage.

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*Brimblecombe and Ramer have disputed the meaningfulness of "air changes per unit time"[14]. For tight, diffusion controlled cases, it is only irrelevant. As long as the term is recognized as a short hand for flow rate of air divided by the folume of the container it is convenient for convection. It has never implied the passage of a distinct parcel of air across the container.

3-4 cm

1-2 cm

Module

50%

0%- 100%

3-4 mm

Figure 5 Typical tube diameter for distribution of RH controlled air from module to display cases. Diameters range from 3-4 cm for main supply pipe to 3-4 mm for medium size display cases.
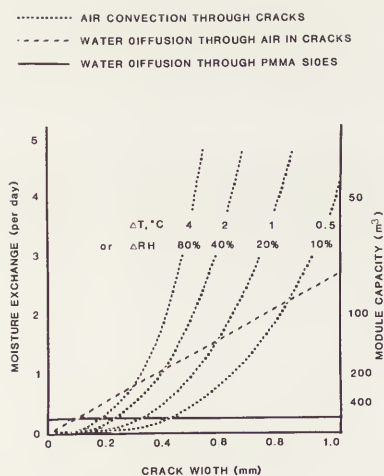
Figure 6 Moisture transfer mechanisms governing air leakage of display cases. Crack width determines which mechanism dominates.

The table below illustrates how many cases the module can therefore supply.

Typical Crack Widths	Natural Case Exchange ΔT = 1°C or ΔRH = 20%	Maximum Module Controlled Volume	Number of cases of size: 0.1m 1m 10m
less than			
0.15mm	0.3 per day	600 m^3	6,000 600 60
0.4 mm	2 per day	100 m^3	1,000 100 10
1.0 mm	15 per day	10 m^3	100 10 1

Simple measures using home "weather proofing" materials can lower crack widths to 0.4 mm or less. Thus, one can assume the module will handle at least one hundred 1 m^3 cases, or ten 10 m^3 cases. If a user finds the module cannot control this many cases, it will be cheaper to weather strip the cases than to build more modules.

Air flow to each case is controlled by the final short length of tube to the case. Most of the air pressure drop occurs across this last piece of tubing. Charts are provided by CCI that correlate the air flow desired with the length and diameter of this final tube. The charts also cover situations where significant pressure drop occurs before the last piece of tubing. Pressure can always be checked with a simple water manometer made from a bottle, stopper and piece of tube. (The maximum pressure of 1.7kPa is equivalent to a 17 cm water column).

Prior to final blueprinting, the prototype had been installed for over a year in a hall of the National Museum of Man, Ottawa. It was connected to nine large cases (80 m^3) spread over 300 m^2 of floor space. Installation took one person one week. Another week was spent filling all externally visible gaps with sealant or weatherstrip (2 people).

One such case was monitored by a hygrothermograph installed within for 2 months. It was 2 m x 2.5 m x 0.8 m with a light box on top, four glass sides and a wooden base. Air flow to this case was 4 acd.

A peculiarity of this hall was that all electrical power was turned off with the lights, including the wall outlet to the module. The module thus operated only about 14 hours per day. Even with this restriction, case RH was well controlled. Figure 7 shows case RH during start up of the module. It begins at the early spring value of 35% RH (as much as the building will stand) and rises to an equilibrium near 47% RH. Module output was

CASE INTERIOR RH DURING START-UP
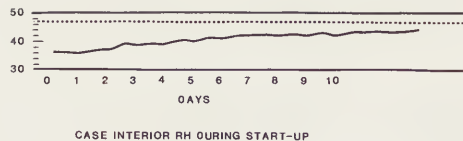
Figure 7 Hygrothermograph chart showing the RH inside a case controlled by the module. The period is for the first 2 weeks after installation. Subsequently, RH is continuously maintained at set-point with variations of no more than ±3%.

50% RH; the 3% discrepancy is due partly to overnight leakage and partly to case heating. Fluctuations due to nightly shutdown of the module are evident, but they are small. The case contents buffered RH change overnight, as expected. The rise time of the case was about ten days. If the module had been operating 24 hr/day, rise time would have been about 6 days and the final RH discrepancy would have been smaller, perhaps 2%. The system is slow to react – if the module output failed, it would take several days for conditions in the cases to respond. An alarm or daily monitoring of RH output of the module would catch a malfunction long before case RH suffered. In contrast, whole building RH control can fail in less than one hour. The module exploits intrinsic case buffers and simply augments RH over the long term.

The module components cost about $1,500. It is designed so that a competent craftsman can build it. Most of the fabrication is with 6 mm polymethylmethacrylate, a material many museum technicians are familiar with. Complete blueprints and assembly manual are now available from the institute*. Negotiations are underway to licence a manufacturer in Canada. If these are successful, price for an "off the shelf" unit will probably be at least Can. $5,000. Equivalent normal silica gel sufficient to stay within a 10% RH annual fluctuation (in Ottawa) would be about 3,500 kg at a cost of Can. $25,000. A gel three times as efficient but at double the cost per unit weight would only lower the cost to $15,000. The cost of retrofitting false bottoms, dismantling the artifacts, etc. would be considerable. The module is obviously cheaper than complete building control. As with any centralized RH control supply, Rh uniformity from case to case is only as good as temperature uniformity from case to case, however, the module will accomodate all temporal fluctuations of temperature, i.e. hourly, diurnal, seasonal.

Conclusion

Humidistatic controlled heating and the relative humidity control module, both conceived and developed at the Canadian Conservation Institute, are two new methods of RH control for museums and art galleries. Although they have received only limited testing, the results acquired so far are extremely promising. Their exceptional performance during field trials indicate that they are viable and cost-effective alternatives to traditional RH control methods.

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A COOLED DISPLAY CASE
FOR GEORGE WASHINGTON'S COMMISSION

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SUMMARY

A cool display case was made for a vellum document. A close fitting airtight container was used. This maintained a nearly constant relative humidity on cooling, but care was needed to minimise temperature gradients. Thermoelectric coolers were used. The case performed satisfactorily for one year with no change in internal moisture content.

Introduction

The Museum of American History in Washington, DC recently put on an exhibition about the life of George Washington, which included the commission, written in 1775, appointing him Commander in Chief of the Continental Army. The Library of Congress, which lent the document, asked that it be kept at about 16°C, some six degrees cooler than the museum gallery, and at 40-50% relative humidity. We designed and built a case to display this piece of vellum during its year on exhibition.

We used the simplest possible method: sealing the document in a small airtight container and cooling it by means of the Peltier effect, which is the absorption or emission of heat when an electric current passes across the junction of two dissimilar conductors.

A close fitting, airtight enclosure has many advantages for the temporary exhibition of flat pieces of vellum or paper. It can be designed to maintain a nearly constant moisture content and a safe relative humidity. It impedes unnecessary handling, excludes air pollutants and gives good protection against flood, fire and vandalism.

The only unusual dangers come from the cooling system, which brings electricity into the case, and from the possibility of air leakage into the container which would cause a dangerous rise in relative humidity around the document.

The climate inside a cooled box containing paper

The document is vellum but the backboard and mat, which together make up most of the weight of the assembly and therefore most of its moisture content, are of paper. Vellum and paper react similarly to changes of RH and of temperature so the following discussion is based on the behaviour of paper made from cotton cellulose, for which more data are available.

Paper always contains some water loosely bound within the fibres. The amount usually depends on the temperature and on the water vapour content of the surrounding air. At room temperature paper contains thousands of times more water than an equal volume of air, so in a sealed box full of paper it is the paper which controls the relative humidity of the surrounding air, if both are at the same temperature.
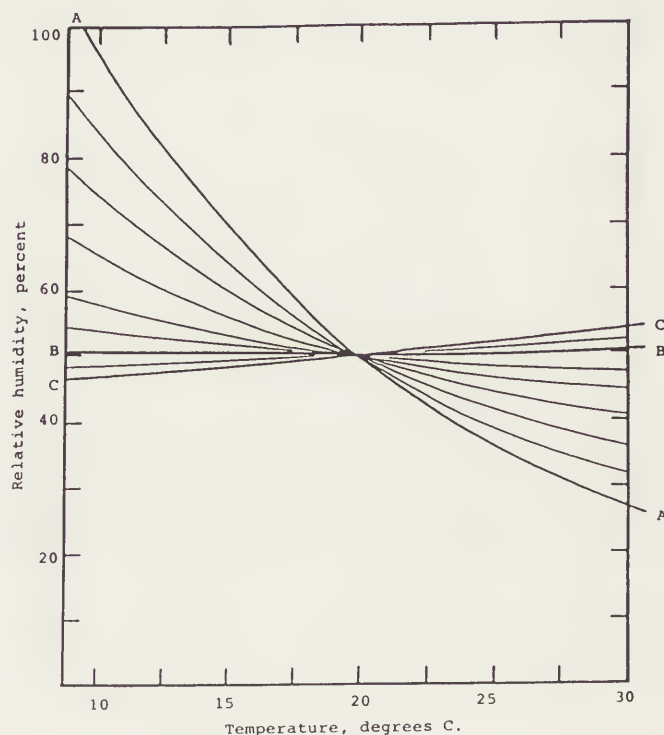
Figure 1. Temperature and relative humidity within a sealed box containing cotton and air in various proportions, originally conditioned to 50% RH at 20°C.

If the box contains only air. The RH rises with falling temperature (curve A), reaching 100% at 9.5^{o}C.
If the box is stuffed with cotton the RH in the small residue of air falls slightly with falling temperature (curve C).
Perfect compensation is provided by 0.6 litres of air for every gramme of cotton (curve B).

Imagine a box containing air and paper equilibrated to 50% relative humidity at 20°C. The box is sealed and the temperature allowed to change slowly. Figure 1 shows what happens to the RH inside.[1] If the box is stuffed with paper, leaving hardly any room for air, the RH moves along curve C. The paper is imposing on the space around it that RH which is now in equilibrium with the amount of water the paper contained at the moment it was sealed up, the residual air having scarcely any water content of its own. Curve A shows how the RH would change if there were no paper in the box. If there is some paper and plenty of air the influence of each on the other leads to an intermediate course: the almost horizontal, almost straight curve B corresponds to one gramme of paper to each 0.6 litres of air. A container with more than about one gramme of paper per litre of air enjoys a reasonably stable RH as the temperature varies, and this rule of thumb holds good over the whole range of ambient temperature.

This happy condition applies only to a slow temperature change imposed uniformly on paper and box. This is what we aimed to do with George Washington's Commission but because the container was cooled from below and most of the heat gain was through the upper surface some small permanent temperature gradient across the container was inevitable. We also had to design for accidental sharp changes in ambient temperature. How would the sealed box react?

Suppose that the document in its paper mat remains at $20^{\circ}C$ while one wall is at some different temperature. The concentration of water vapour will remain unchanged and uniform everywhere in the box, so the RH at any point will be determined by the temperature at that point, according to curve A in figure 1. Paper will neither gain nor lose water to compensate for this change if it remains at a constant temperature. It "disappears" from the climate controlling process. It is important to realise that absorbent materials such as paper or silica gel only function as RH buffers if they are at the same temperature as the air, or object, which is to be buffered.

If the temperature should fall to below $9.5^{\circ}C$ at any wall of the container while the paper remains at $20^{\circ}C$, the RH at that wall will reach 100% and water will condense. This reduces the water vapour concentration in the air and now the paper will release more water vapour, which will again turn to dew on the cold wall. This distillation process will tend to dry the paper. Water from the cold wall may flow to the paper and soak parts of it. The result will be brown water marks.

From this analysis of the closed box with paper we developed a specification for the display case.

To prevent mould growth the RH must always stay below 65% everywhere in the case. This means that no part may be more than about four degrees cooler than the paper during steady operation. We allowed ourselves a maximum two degrees difference between the document temperature and the lowest temperature at the walls of the sealed case when it was in steady operation. The estimated temperature gradient across the assembly of document and mat was one degree. This would cause a 3% RH range in the interstitial air and a negligibly small variation in moisture content.

The display case must be double glazed. In the event of catastrophic cooling of the gallery the other exhibits will need first aid first because the danger to our exhibit is lessened by good insulation and by its coolness.

Unexpected sudden warming of the case should cause no climatic problems at all because the walls are insulated and the lid contains no water, so the reverse movement of water from the walls and nearby air into the paper can only occur to a trivial extent.

An important aspect of climate control in a cooled container without mechanical RH control is that it must be perfectly air tight. Any leakage of warm air into the container will cause an increase in moisture content of the paper. The incoming air increases in RH as it cools down and the paper absorbs water from it. For example air at $20^{\circ}C$ and 50% RH reaches 65% RH if

cooled to $16^{\circ}C$. We allowed for some leakage and put extra paper in the enclosure to increase the RH buffering capacity. The most important precaution however was to put a humidity sensor in the enclosure. This was not just to measure relative humidity during correct operation, which we confidently assumed would conform to theory, but to detect leakage of air.

Another important design condition was that materials used within the case should not release harmful gases. The common practice of using new plywood and fresh paint in showcases for temporary exhibitions causes release of vapours of formaldehyde, acetic acid and other organic pollutants. Airtight enclosures are a positive conservation measure in such an environment.

As a further guard against pollution the card strips put in the case as a buffer against the effects of air leakage contain calcium carbonate to absorb acid gases.

The other features of the design were that it must allow easy removal of the object in an emergency without trailing cooling equipment and wires along with the precious container. It should resist fire for as long as possible because fire is the main hazard to any case containing electrically operated technology. The sealed case will prevent smoke damage to the paper and it will of course be waterproof.

The Final Design

The most demanding of these various requirements was the small temperature gradient allowed. This was difficult to meet because the commission was shipped from the Library of Congress matted and sandwiched between 6 mm acrylic sheets, which are not good heat conductors.

The entire system is illustrated in a cut away diagram, figure 2. The document assembly was laid in an aluminium tray with a 12 mm thick base and even thicker sides. This conducted heat from the two tiny (20 mm square) cooling devices so well that the inside walls and floor were of uniform temperature within one degree. The tray was laid horizontally to prevent convection currents. Sides and base were lined with cork insulation 25 mm thick. The glass lid was supplemented by the acrylic glazing of the showcase which prevented warming draughts. When the tray was seven degrees below ambient temperature the document was more than six degrees below.

Our other main concern was to prevent air leakage. We used orthodox vacuum technology. A viton O ring lightly greased with hydrocarbon lubricant lay in a square section groove in the aluminium wall. A lid made of armoured glass lay on the aluminium, slightly compressing the O ring. The glass was held down by fourteen spring steel clips. These were made easy to remove because the tray and glass were heavy and in an emergency one could move faster clutching only the inner sandwich of acrylic sheet.

The tray rested in the cork insulation which in turn sat on four wooden posts attached to the showcase. The entire tray could therefore be lifted out once the showcase lid was removed. The only part of the cooling system that came with it was a slimy residue of the silicone grease used to give good thermal contact between the thermoelectric coolers and the tray.
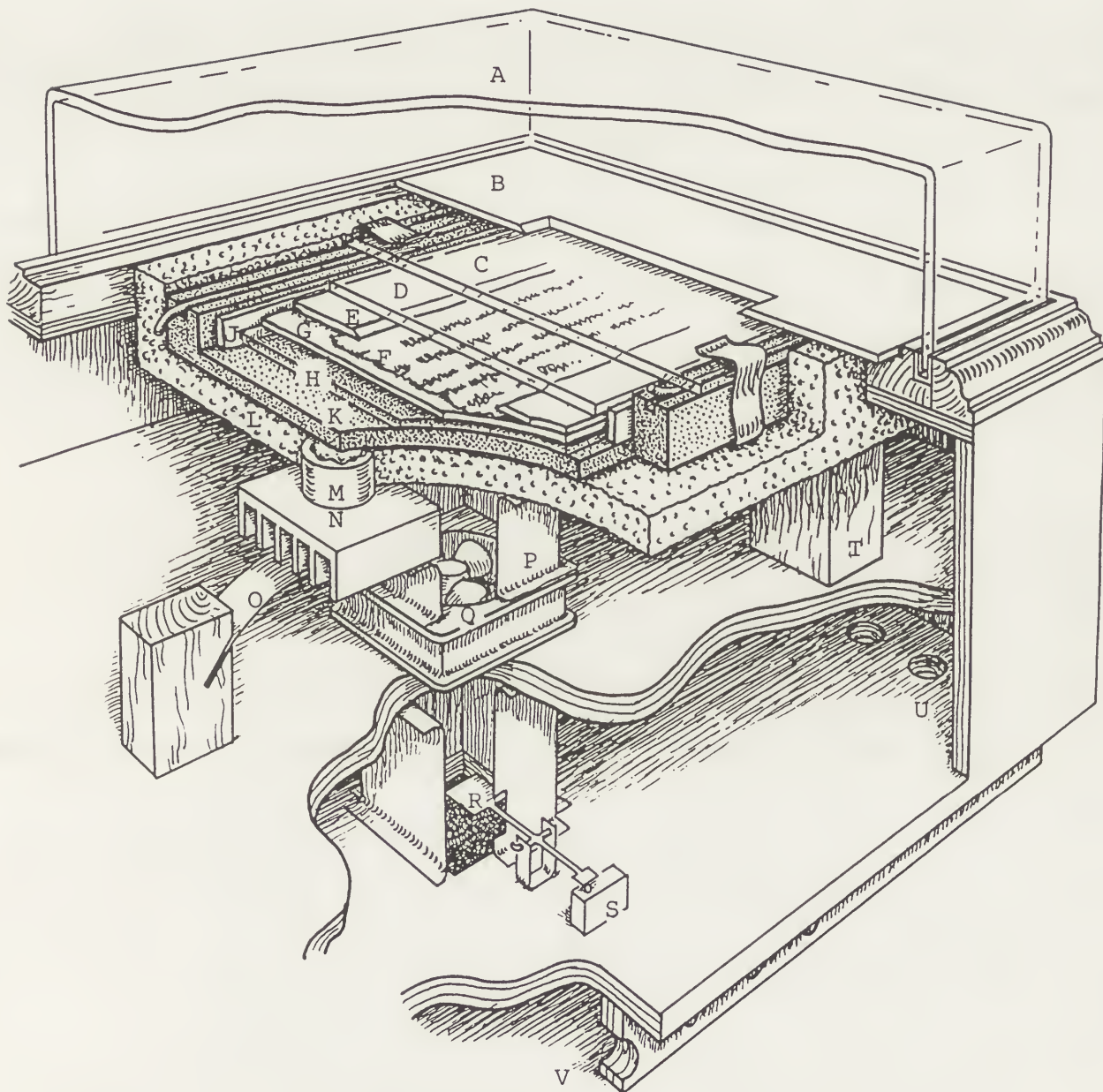
Figure 2.

Cut away diagram of the display case. The document F is enclosed by mat E and back board G. All this is sandwiched between Plexiglas sheets D & H and bound together with adhesive tape round the edges. This sealed assembly lies in the aluminium tray K and is covered by armoured glass C. A viton O ring lies in a groove round the edge of the tray. The glass is pressed down onto the O ring by spring steel clips. The tray is insulated by cork L. All of this is supported within the showcase by four wooden blocks T so that it can be lifted out easily once the Plexiglas case top A has been removed. A frame B conceals the cork insulation and steel clips.

The thermoelectric coolers M and the heat dissipating fins N are pressed up against the aluminium tray by a spring O. The duct P directs cooling air from the fan Q over the fins and eventually out through the holes U in the base of the case. Air comes into the case through holes V and is drawn up past the hinged plate R, which operates switch S when it is pressed up by the flow of air.

The Cooling System

The danger of creating rapid temperature changes and steep gradients caused us to design a cooling system barely adequate for the job when running flat out. This simplified the control system greatly. The cool case hung seven degrees below the controlled temperature of the gallery. The cooling system can fairly easily be altered to work in a variable environment but it would need more power and it would be less efficient.

We used two thermoelectric coolers.[2] These are made up from short lengths of two different semiconductors alternating in series. When a current is passed every second junction gets cold and those in between get hot (Peltier effect). The junctions are arranged in a compact slab, 20 mm square by 4 mm thick, so that one side gets hot and the other side cold.

Each of the two coolers was clamped between an aluminium cylinder on the cold side which penetrated through the thermal insulation to the tray and conducted heat away from it, and a set of aluminium cooling fins on the hot side. The fins were cooled by a stream of air as shown in figures 2 and 3. The circuit diagram and the various safety devices are shown in figure 3.

The heat loss from the insulated tray was about five watts. The total power going into the case to supply the coolers and fan was nearly forty watts. Thermoelectric coolers are not very efficient and a further loss of efficiency was caused by water condensing on the cold surfaces close to the coolers which were below the dew point temperature of the air. We did not discourage this process because it functioned as a thermostat preventing cooling of the tray below the dew point, which would be undesirable because dew would condense on the outside of the glass cover and obscure the document within. We eventually used a wax resin mixture around the coolers to prevent condensed water from corroding them. The water migrated to the cooling fins and evaporated into the air stream.
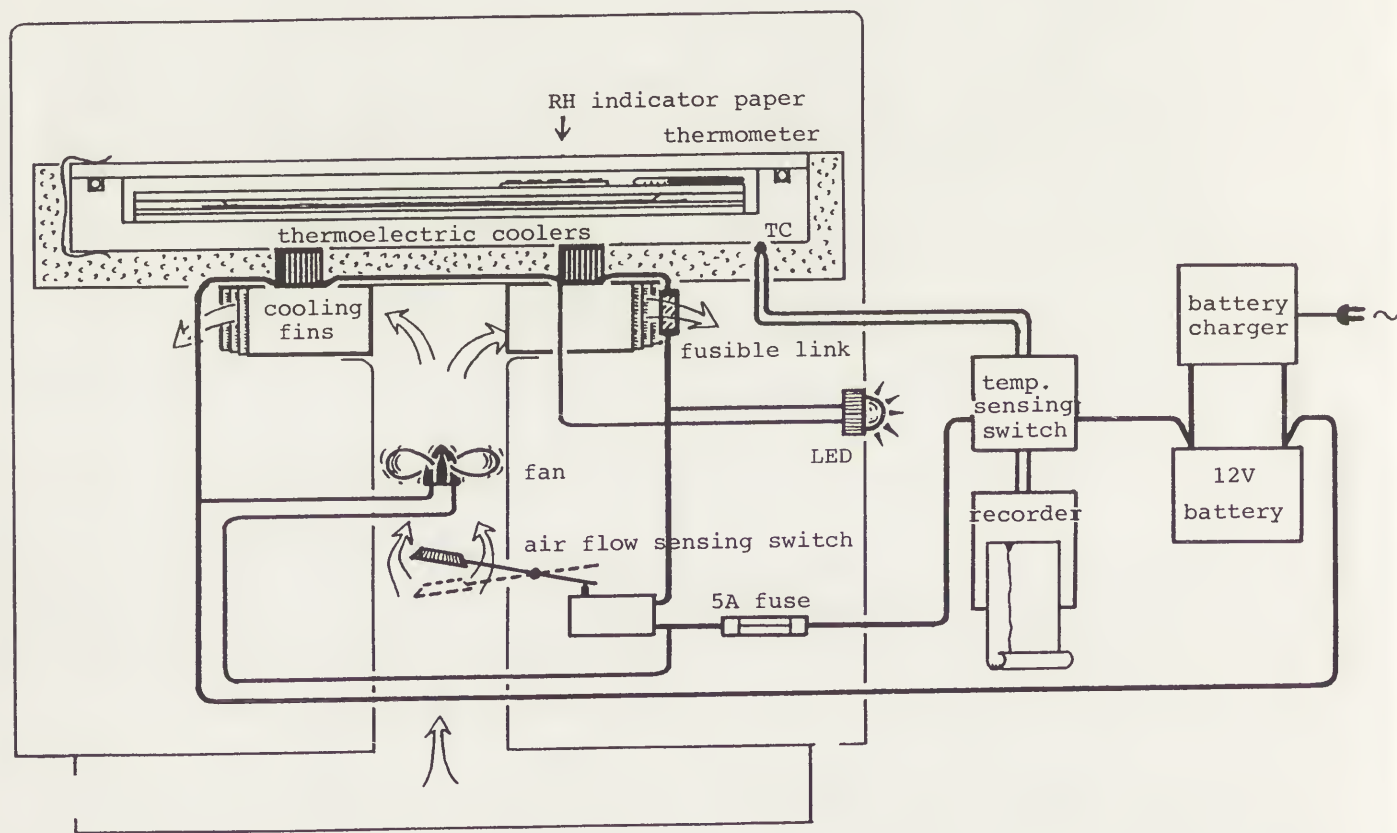
Figure 3 Circuit diagram. The thick line is the main cooling circuit. The battery charger and battery provide both a reserve of power and a constant voltage source. The temperature sensitive switch breaks the circuit if the tray warms above 25ºC. The 5A fuse protects against overheating due to a short circuit in the display case. The air flow sensing switch closes the main circuit only after the cooling air flow is established. If this switch sticks shut a fusible link breaks the circuit if the cooling fins get hot. Correct operation is shown by a small light emitting diode. If either cooler fails to conduct the light goes out. If one cooler short circuits the light goes out, if the other cooler short circuits the light burns out. The temperature of the tray is continuously recorded. The temperature above the document is shown by an alcohol in glass thermometer. Leakage of air into the case is revealed by the rise in RH indicated by the colour change of cobalt salt impregnated paper.

This cooled case operated for about a year. It failed twice. Once the fan failed to re-start after a power failure and had to be prodded into action. Then one thermoelectric cooler failed through corrosion by condensed water. Both coolers were replaced and protected by wax-resin mixture. The result of each failure was a slow warming of the exhibit to room temperature and no damage was done. At the end of one year the case was removed from exhibition. When the glass lid was raised the cardboard strips, which had been put in to protect the document against moisture absorption through leakage of air, were quickly removed, put in a polyethylene bag and weighed. They were then allowed to condition to equilibrium with air at 50% RH, 20°C and re-weighed. There was a small weight gain from which we deduced that the document had been maintained in an atmosphere of about 40%-45% RH at 16°C. It went in at 50% RH at 20°C. There was evidently very little leakage because air exchange with the gallery would have pushed the equilibrium RH within the case towards 70% at 16°C.

References and Notes

1. Data for figure 1 were obtained from the psychrometric chart published by the Institute of Heating and Ventilating Engineers and from: A. R. Urquhart & A. M. Williams, The effect of temperature on the absorption of water by soda-boiled cotton. J. Textile Institute 15 (1924) T559-573.

2. A. F. Joffe, Semiconductor thermoelements and thermoelectric cooling. London 1957.

Technical details: The document measures 500 x 240 mm. The inside of the aluminium case measured approximately 750 x 450 x 50 mm. The total weight of paper within the enclosure was 400 g, the air volume was about 0.004 m^3. The insulation was 25 mm of cork round sides and base.

The thermoelectric coolers operated at 6V, 2A each. They were made by Melcor/Materials Electronic Products, 922 Spruce Street, Trenton, New Jersey 08648 USA. The cooling fins had an area of about 60,000 mm^2. The cooling rate of the box was 5 degrees per hour diminishing asymptotically to zero at 7 degrees below ambient.

The overheating detector was a copper-constantan thermocouple connected to an Omega controller, model 50 T (Omega Engineering Inc. Stamford, CT, USA). This controller was used as a protective switch but it can be used as a thermostat.

The axial fan moved 2 m^3 of air per minute.

DESHUMIDIFICATION D'UNE VITRINE PAR UN SYS-TEME DE CHAUFFAGE

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Deux vitrines contenant des métaux archéolo-giques sensibles à l'humidité ont été modi-fiées et chauffées de manière à réduire le taux d'humidité.

Les récents travaux de restauration effec-tués en Italie (à Crotone, ville au bord de la mer) sur une centaine d'objets archéolo-giques en fer datant du Vème Siècle av.J.C., ont rendu indispensable la création d'un mi-lieu sec, approprié à la conservation des métaux.

Etant donné l'état avancé de la corrosion des objets, la nécessité de mettre au point un micro-climat avait été examinée dès le début. Cette opération est devenue indispen-sable lorsqu'on a constaté des points de cor-rosion active sur un certain nombre d'objets, restaurés depuis quelques semaines et ayant pourtant été traités avec un stabilisant de la corrosion (Fertan).

Les objets, comprenant des chaines de diver-ses dimensions et des outils de travail, devaient être exposés dans des vitrines déjà existantes au Musée de Crotone. Celles-ci ont dû être modifiées et climatisées de ma-nière appropriée avec des moyens simples et peu de manutention.

Deux vitrines ont ainsi été isolées et tou-tes les fissures et zones de passage de l'air ont été obturées à l'aide de silicone trans-parent de façon à réduire, dans la mesure du possible, la pénétration de l'air salin hu-mide.

Afin de réduire le taux d'humidité relative, on est parti du principe selon lequel, dans un volume déterminé d'air, l'augmentation de la température entraine la diminution de l'humidité relative : il a donc été décidé de maintenir un taux d'humidité relative in-férieur à 50 pour cent (comme l'indiquent les normes pour la conservation des métaux), tout en restant dans les limites de tempéra-ture acceptables.

L'air a été chauffé par une faible résis-tance électrique et un système de légère ven-tilation, destiné à en uniformiser les condi-tions, a été installé dans la partie infé-rieure et non visible de la vitrine. L'ensem-ble a été relié à un humidostat situé dans la partie médiane.(voir fig. 1)

Chaque fois que l'humidité relative interne dépasse 45 %, l'humidostat met en fonction la ventilation tiède et l'air est chauffé pour atteindre la valeur de 40 % environ.

Ensuite, le système s'interrompt et reprend automatiquement, si nécessaire.

Les conditions dans les vitrines et à l'exté-rieur de celles-ci ont été contrôlées simul-tanément avec des thermohygrographes pendant plusieurs périodes de l'année ; les résultats ont donné des taux optimaux en ce qui concer-ne l'humidité, avec une augmentation de la température variant de 2 à 9 degrés centi-grades par rapport à celle de l'extérieur.

L'évolution a été enregistrée sur des diagram-mes de thermohygrographes ; les courbes indi-quent que l'augmentation de la température interne atteint rarement + 9° par rapport à la température extérieure et la plupart du temps, la différence reste entre 2 et 6°centi-grades. (voir fig. 2 et 3)

Dans la vitrine plus grande (2,55 m^3), l'ab-sorption d'énergie est de 365 watts (15 watts pour le ventilateur et 350 watts pour la ré-sistance), alors que dans la vitrine plus petite (2,00 m^3), elle est de 315 watts (respectivement 15 et 300).(voir fig. 4)

Chaque vitrine est munie de deux témoins lumineux situés à l'extérieur, sur le tableau de commande, avec l'interrupteur général et le fusible. Le premier témoin indique le rac-cordement, alors que le second s'allume seu-lement quand la ventilation tiède est en action. L'opérateur peut ainsi contrôler facilement le bon fonctionnement du système. A l'intérieur de chaque vitrine, un hygro-mètre indique le taux d'humidité relative.

Cette solution, simple à réaliser, et en fonc-tion depuis huit mois, semble avoir stabilisé parfaitement l'état de conservation délicat des objets mentionnés et pourraît en même temps correspondre aux exigences d'un musée disposant d'un personnel spécialisé limité.

(voir diagrammes, schéma de raccordement élec-trique et photo).
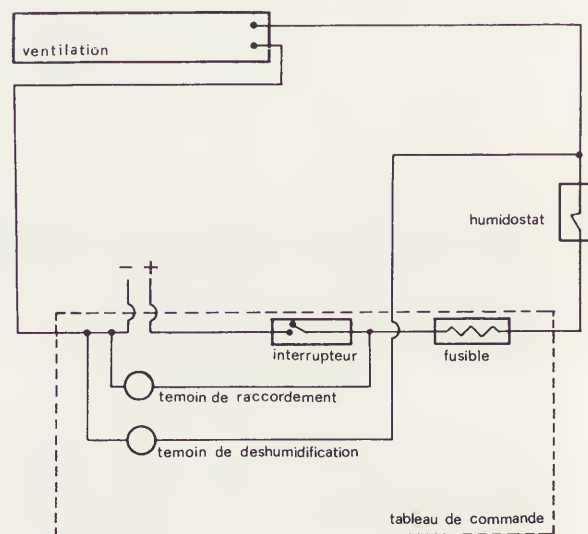

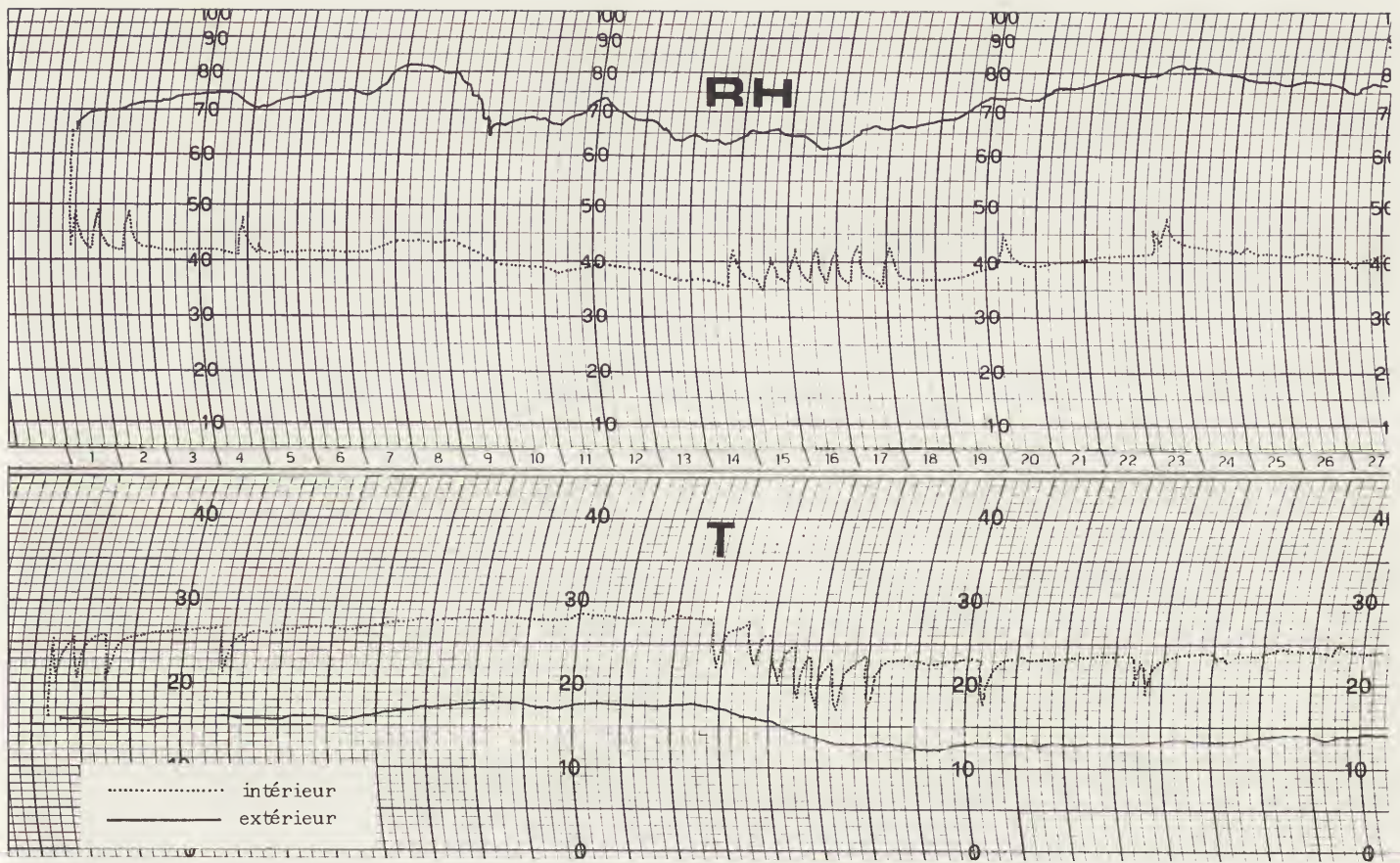fig. 1 : raccordement électrique

fig. 2 : conditions à l'intérieur et à l'extérieur de la
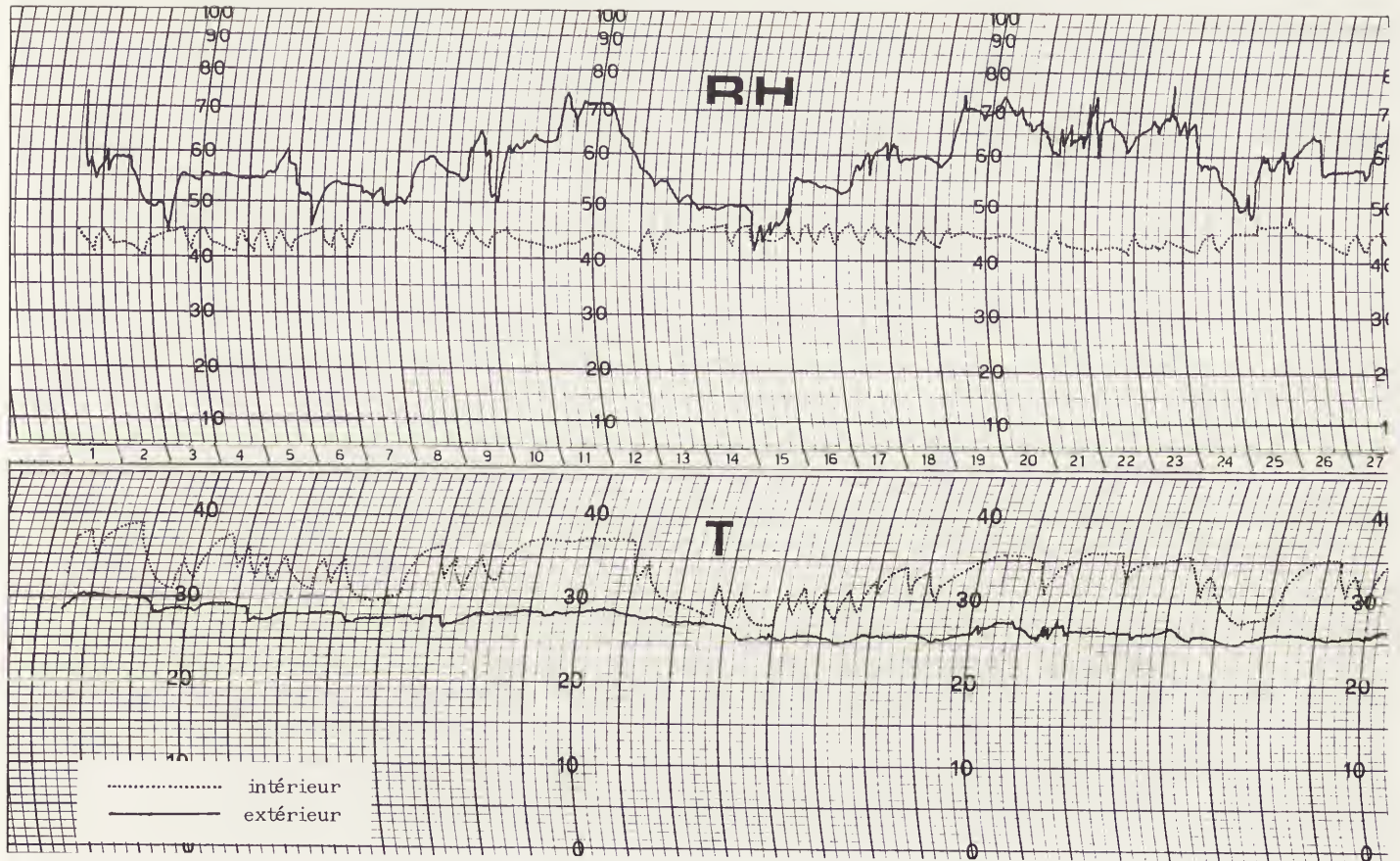vitrine durant la période du 25 novembre au 10 décembre 1983.

fig. 3 : conditions à l'intérieur et à l'extérieur de la
vitrine durant la période du 21 août au 5 septembre 1983.

fig. 4 : photographie d'une vitrine

THE DESIGN AND CONSTRUCTION OF TWO HUMIDITY-
CONTROLLED DISPLAY CASES

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SUMMARY

The design and construction materials of two
museum display cases containing a humidity
buffer are described. One case, adapted from
an existing design, acts as a storage/dis-
play case for three-dimensional objects. The
other is a specially designed case for the
display of a panel painting. The design cri-
teria linking the two systems of humidity
control are discussed.

1.0 Introduction

Growing interest has been shown in various
methods of stabilizing the climate within
display cases. Particular study has been
given to non-mechanical systems of humidity
control which employ a humidity buffer.
Recent work has demonstrated that the behav-
iour of such systems depend, in part, on the
extent to which the case deters leakage (1).
In drawing attention to the merits of well-
constructed display cases, this paper dis-
cusses the various features of case design
and construction which contribute to effec-
tive humidity control.

2.0 The Display Case for Three-Dimensional Objects

The Study Reserve Area of the Sainsbury
Centre for Visual Arts contains the various
study collections belonging to the Univer-
sity of East Anglia. Situated on a mezzanine
level between the School of Fine Arts and
the main gallery, the area is readily acces-
sible to lecturers and students as well as
the general public. By housing works of art
which might normally be kept in the basement
store, the mezzanine acts as both a storage
and display space.

As part of a re-organization of the Study
Reserve Area in 1983 (while the author was
employed at the Sainsbury Centre), a new set
of cases was specially designed to accommo-
date three-dimensional objects from the col-
lections. The features of the original set
purchased for the Sainsbury Centre, like
many commercially available models, offered
little scope for environmental control. The
sliding glass doors provided no barrier to
the rapid humidity changes which can occur
in the building. Equally, dust and atmos-
pheric pollution entered the case interiors.
The decision to re-organize the mezzanine
area provided an opportunity to advise on a
more effective case design (2).

2.1 Case Design and Construction

Constructed from metal and glass, each of
the fourteen new cases has a volume of 1.9
cubic metres (Figure 1). The face panels,
consisting of polished plate glass 10mm
thick, are set into a groove in the metal
framework except at the top of the case.
Here the edges of the four panels which form
the top and three vertical sides are bonded
with a strong translucent glass cement. The
framework itself is of steel which is given
a grey stove enamel finish to match the
other display cases in the Sainsbury Centre.
Artificial lighting is not installed in the
cases. Low-voltage lamps attached to elec-
trical tracks mounted in the ceiling pro-
vide illumination from above. Each case has
two compartments in which glass shelving can
be erected for additional display space.

One complete wall of the case becomes a
sliding door panel to allow access to the
interior. When shut, the door panel fits
flush against its adjoining members. A sil-
icone resin along the edges of the adjoining
sides acts as a gasket between these sides
and the perimeter of the door. This sealant
makes the display case dustproof and retards
the leakage rate between the interior and
its surroundings. In addition, magnets
placed within the case's framework improve
the snug fit. Also concealed within the
door's framework are two pin tumbler cylin-
der locks which keep the case secure when
closed.

After unlocking, the door panel is free to
move in three directions: first forward, and
then left or right along a track. The mech-
anism enabling the door to make these move-
ments lies in a cavity between the bottom of
each compartment and the suspended floor. A
movable metal rod, mounted perpendicular to
the track, enables the door panel to be
pulled approximately 5cm away from the rest
of the case. In this position the door is
able to slide along the track in either
direction until the display case is half-
open (as shown in the figure). With adjust-
ment, however, it is possible to remove the
door panel completely for the installation
of large objects or glass shelving.

2.2 The System of Humidity Control

The system of humidity control for each case
is compatible with the one developed for the
standard-size display cases in the Sainsbury
Centre (3). The cavity which houses the
mechanism for the sliding door panel also
acts as a centre for humidity control within
the upper and lower compartment. As it was
not possible to construct an independent
access door to the humidity buffer, it is
necessary to lift the suspended floor of
each compartment to reach the buffer.

The buffering agent, regular density silica
gel, is stored in muslin bags which are
placed across the floor of each cavity. The
bags, made proportional to the dimensions of
the floor, allow both easy handling and max-
imum surface distribution of the buffer. By
means of a hook and pile fastener strip
(Velcro), the bag is opened or sealed along
one side. This allows the silica gel to be
replaced with either a new preconditioned
batch or a different buffer. At present,
2.5kg (dry weight) of silica gel is stored
in each bag: three bags in the upper cavity
and four in the lower one. (This is due to
the difference in placement of the door
mechanism for each cavity).
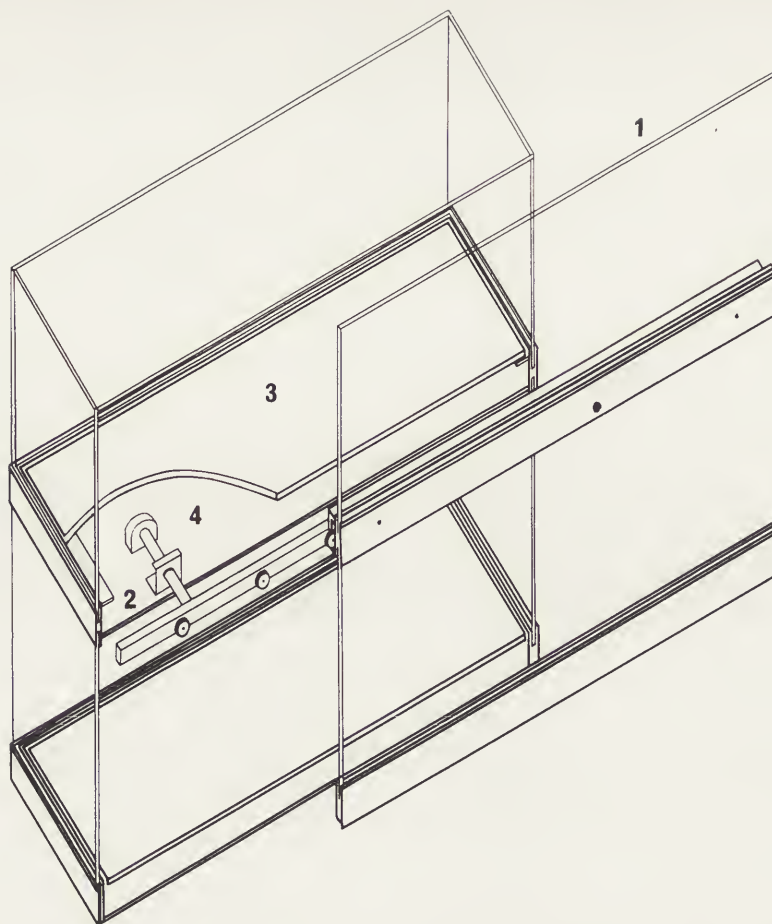
Figure 1. Simplified drawing of display case for three-dimensional objects. 1) sliding door panel; 2) door mechanism; 3) suspended floor; 4) cavity. The lower compartment of the case has a similar arrangement.

To facilitate air circulation between the buffer and the display volume of each compartment, the wood board which acts as the suspended floor is modified. Before being covered with fabric, the board, a varnished birch veneer plywood, is drilled with a regular pattern of holes each approximately 5mm in diameter. In addition, to enhance air circulation around the perimeter of the suspended floor, the depth of the board is rebated.

Monitoring of the relative humidity inside the cases is in its initial stage at present. A preliminary study focused on the environmental conditions experienced in a case containing ethnographic material. Silica gel preconditioned to 55% RH was installed in the case in the proportions described above. A hair hygrometer was used to monitor the relative humidity. Although diurnal variations in humidity were recorded on the mezzanine level, the relative humidity inside the case remained stable. It is hoped a more comprehensive long-term study will be carried out to assess the effect of seasonal humidity variation on the environmental stability of the case interior.

3.0 The Display Case for a Panel Painting

Among its various roles, the Area Museums Service for South Eastern England (AMSSEE) provides technical assistance for its member museums in the region. The AMSSEE Painting Conservation Studio, during treatment of a 17th century Netherlandish panel painting, asked the author to advise them on the design of a humidity-controlled display case for the painting.

3.1 Design Criteria

The initial stage of the project involved listing the design criteria appropriate to the request. It was jointly agreed that, as much as practicable, the case design should not interfere with the viewing of the painting. It was therefore decided to place the painting in the case and to extend the rabbet of the painting's frame in order to accommodate the case behind the frame.

A non-mechanical method of climate control involving the use of a humidity buffer was felt most suitable for a small museum without a conservation department. To enable the museum to have direct control over its painting, it was envisaged that the museum staff would be instructed on the monitoring of the case and the replacement of the humidity buffer.

An essential design criterion was a close-fitting case which could deter rapid air exchange between the case interior and its surroundings. This would enable the buffer to depress RH variation inside despite daily and seasonal fluctuations within the gallery.

To enable the buffer to work most effectively, the interior design of the case required adequate air circulation between the painting and the buffering agent. In addition, distribution of the buffer over a large surface area was considered important.

In consideration of the museum staff, ease of access to the buffer as well as ease of handling during its replacement were deemed desirable. It was felt equally important that the painting not be disturbed from its position during this maintenance.

Last, the choice of the appropriate humidity buffer included such factors as:
  a) capable of stabilizing humidity variation at 55% RH,
  b) readily available at a low cost and
  c) compatible in particle size with its method of storage(described below).

3.2 The Case Design and Construction

Before construction of a final prototype, a mock-up was made (4) to the required dimensions of 95cm x 50cm x 15cm (Figure 2). For the outer framework and back, 5mm PVC (polyvinyl chloride) sheeting was chosen as an inexpensive and easily fabricated material. The joins were chemically welded. The front of the case was glazed with acrylic sheet which was secured to the outer framework with a silicone sealant, after which the glazing's edges were covered with PVC moulding.

A removable lid gave access to the case interior. Made from the same material as the outer framework, the lid was aligned by eight bolts which projected from the body of the case. By unfastening a wing nut atop each bolt, the lid could be easily removed. The lid overlapped the outer framework to ensure a close fit between it and the body of the framework.

A pair of channels were mounted on either side of the interior of the case adjacent to the lid. Into these could be slipped an acrylic sheet which would act as both a mount and support anterior to the painting. A substitute panel of approximate thickness replaced the painting in the mock-up. To secure the substitute panel to the acrylic sheet, neoprene cylinders were used. Each cylinder was rebated to accommodate the thickness of the panel.

The lid of the case formed an integral part of the cartridge which housed the humidity buffer, in this instance, silica gel. With this cartridge arrangement, one could both reach and handle the humidity buffer easily. Following Thomson's recommendation (5), the cartridge was designed to contain silica gel in the proportion of 20kg per cubic metre of case volume.

To house the buffer within the cartridge, 12 independent modules were constructed. Measuring 15cm x 15cm x 1.8cm, each module consisted of a PVC framework, nylon grid and stainless steel mesh. The cells of the grid permitted even distribution of the silica gel in each module. The mesh acted to hold the buffer within the cells while permitting air circulation to the painting.

The modules were placed between pairs of U-shaped aluminium channels to form a grid pattern measuring 3 x 4 modules in size. This arrangement constituted the cartridge, its top being the case lid and the bottom a
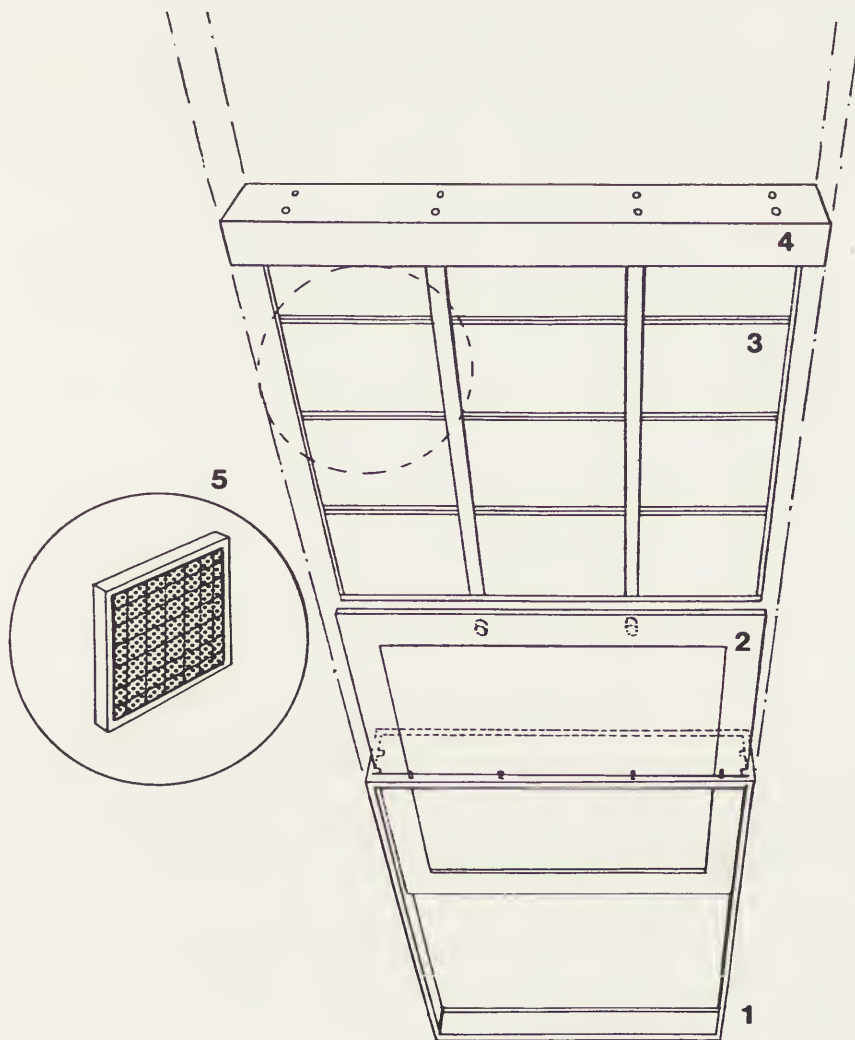

Figure 2. Simplified drawing of the display case for the panel painting. 1) case framework; 2) acrylic mount for painting; 3) cartridge; 4) case lid; 5) silica gel module.

separate U-shaped aluminium channel. This channel was easily removed by unfastening two wing nuts in order that the modules could be replaced when required. A two cartridge system was proposed to enable the museum staff to have a spare set of modules (containing preconditioned buffer) immediately at hand.

Regular density silica gel (2.5mm -6mm particle size) was chosen for use because it was inexpensive, readily purchased and of sufficent particle size to be retained by the stainless steel mesh. The buffer was preconditioned to the desired humidity level, 55% RH, in order to assess the effectiveness of the case design and construction. In a short-term study, the relative humidity within the case was monitored with a hair hygrometer. The experimental results indicated that stable environmental conditions could be maintained. On the basis of these findings, an aluminium case of the same design was constructed with some minor refinements.

3.3 The Refined Display Case

In its present version, the outer framework of the case is constructed from 6mm aluminium sheet, making the weight of the case significantly lighter. The acrylic glazing has been replaced with a 5mm polycarbonate sheet (Lexan). The glazing is fitted into a pair of grooves in the outer framework rather than being covered with moulding.

The lid, now an aluminium plate, is no longer attached to the cartridge. By releasing two pressure fasteners, the lid is removed to gain access to the cartridge within. The cartridge moves in and out of the case on a grooved track, as does the acrylic mount for the painting.

The PVC framework of the modules has been replaced by aluminium. In addition, the same material now constitutes the grid of each module. This enables the humidity buffer to be regenerated and preconditioned in its module. Both the PVC and nylon of the previous set of modules were not able to withstand the heat required for regeneration.

In addition to display of the painting, the robust construction of the case could lend itself to climate-controlled transport. Stable environmental conditions could thereby be maintained throughout a travelling exhibition.

4.0 Conclusion

Although differing in design and construction, both cases make use of basic principles of humidity control. Both cases are well-constructed units which deter rapid air exchange between case interior and its surroundings. Both distribute the humidity buffer over a large surface area to achieve maximum effect. In addition, the buffer is stored in permeable containers in order to facilitate air circulation within the case interior.

Both case designs emphasize ease of maintenance. Within the limits of each case design, both access to and handling of the humidity buffer are made as simple as possible. A practical feature is the standardization of the storage units containing the buffer, a feature which simplifies both preconditioning and regeneration. This is an important consideration when a large number of cases require humidity control.

REFERENCES AND NOTES

1. Brimblecombe, P. and Ramer, B., "Museum Display Cases and the Exchange of Water Vapour", Studies in Conservation 28 (1983) 179-188.

2. The set of cases was designed by George Sexton Associates, Washington D.C. The set was adapted from an existing model manufactured by Glasbau Hahn, Frankfurt am Main, West Germany.

3. Ramer, B., "Stabilising Relative Humidity Variation Within Display Cases: The Role of Silica Gel and Case Design", ICOM Committee for Conservation, 6th Triennial Meeting, Ottawa, 1981, 81/18/6.

4. In addition to the author, the design for the case was made by Brian Hartley, Designer for the AMSSEE (Milton Keynes), and Anna Southall, formerly Conservator of Paintings for AMSSEE. Brian Hartley arranged for the construction of both the mock-up and refined case. The mock-up was made by Polyform Plastics, Leeds.

5. Thomson, G., "Stabilization of RH in Exhibition Cases: Hygrometric Half-Time", Studies in Conservation 22 (1977) 85-102.

STABILIZATION OF RH IN EXHIBITION CASES : AN EXPERIMENTAL APPROACH

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ABSTRACT

The variation of the relative humidity (RH) in an experimental exhibition case containing silica gel has buffer has been monitored over a period of 2 1/2 years. Whereas the RH in the room varied between 20 % in the winter and 70 % in the summer, it remained inside the case within acceptable limits (40 - 58 %). Short time variations were completely eliminated and long time variations were slow and gradual. Our experiment shows, that an exhibition case which contains silica gel does, in regions with low winter and high summer relative humidities, not require maintenance for many years.

1. Introduction

The usefulness of sorbents, such as silica gel, to stabilize the relative humidity (RH) within an exhibition case has been demonstrated in several cases. There are by now a number of papers on this subject, treating mostly "theoretical" aspects (1-5). Only a limited number of publications are relevant to practical applications (5-9). Although this approach seems to be simple and inexpensive it has, so far, not been widely used in museums. The limited application in smaller museums may be due to the fact that curators and restorers are reluctant to accept "theoretical" proofs of the applicability and are waiting for "hard" facts. The aim of this small project, which we carried out between 1979 and 1982, was therefore to answer the following three questions :

1) does this system actually work ?
2) what are the costs ?
3) does the installation need maintenance ?

2. Experimental
2.1 Experimental exhibition case

We used for our experiment a Perspex-box (height 47 cm, length 47 cm and depth 20 cm). The inner faces were lined with aluminium foil to reduce water-vapour-loss through the side panels and to imitate a glass case. As front panel we simply applied a glass plate which was held with a screw-clamp. This arrangement can be, as far as the leackage is concerned, compared to an older museum display case.

2.2 Buffer material

We used silica gel as sorbent (10). Following Thomson's recommendation (1) we placed 800 grams of preconditioned silica gel for a volume of 40.5 l in the case (this corresponds to 20 kilograms per cubic meter). The silica gel formed a layer of approx. 0.5 cm thickness on the botton of the case. The conditioning of the silica gel was carried out over a period of 3-4 weeks at 60 % RH as described in a previous paper (9).

2.3 Monitoring of the relative humidity

The relative humidity inside and outside the box was measured with two hair-hygrometers (11) which were periodically checked with a psychrometer (12). Readings were taken at more or less regular intervals (2-4 days) from April 1979 to December 1982.

2.4 Emplacement of the experimental case

The case was placed in the office of the laboratory. This room is not air-conditioned and shows great variations in RH between summer and winter. These are mainly due to the ventilation situated in the work-area of the laboratory which creates an air-flow from the windows towards the ventilation channel (fig. 2). This situation is far from ideal and we have to take special precautions when humidity sensitive objects are examined and treated.

3. Relative humidity changes in the case

The discussion of the relative humidity variation in the case is best subdivided into two sections :
a) short time stability
b) long time stability.
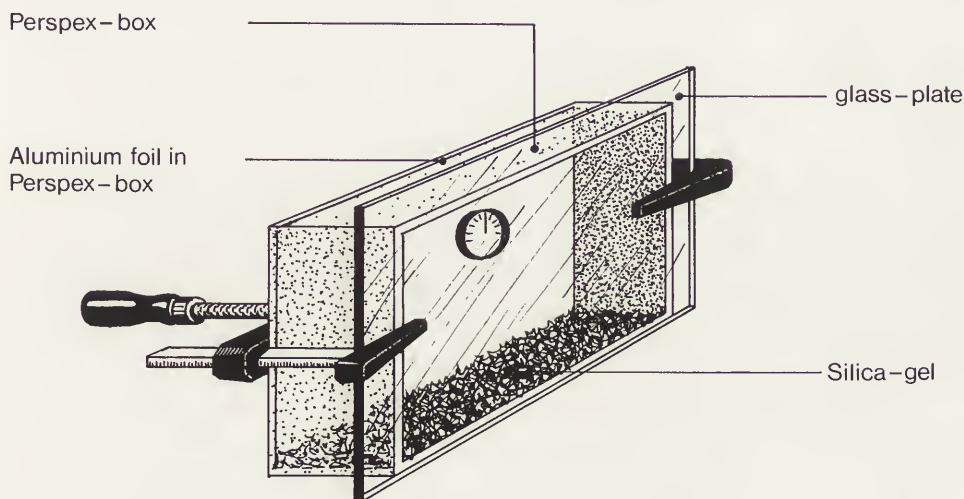
Fig.1 Experimental show case
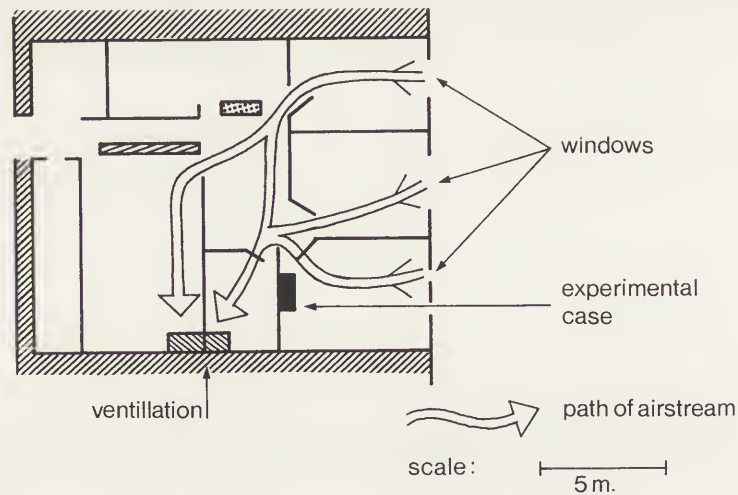
Fig. 2 Plan of the laboratory with location of the experimental case

3.1 Short time stability

The stability of the case for a period of 24 hours and one month is illustrated in figs. 3 and 4. The relative humidity does not change more than 3 % when the case is placed from a RH of 29 % to one of 71 % for a period of 24 hours (fig. 3). Even over one month the stability is very satisfactory. Fig. 4 illustrates the variation observed from the 10th August to the 10th September 1979. Although the external RH varies considerably the RH in the case rises only very gently over this month by 3 %. It is clear that the case is capable of eliminating these short time variations very effectively.

are very slow and gradual indeed. From February to May there is almost no noticeable change at all. At the beginning and the end of the heating period, November to January and June to August, the maximum change in RH is about 5-7 % per month or 0.16 % to 0.23 % per day. Even humidity-sensitive objects are hardly affected by these slow and small variations. We noted with interest that the buffering efficiency of the silica gel did apparently not decrease after more than two years.
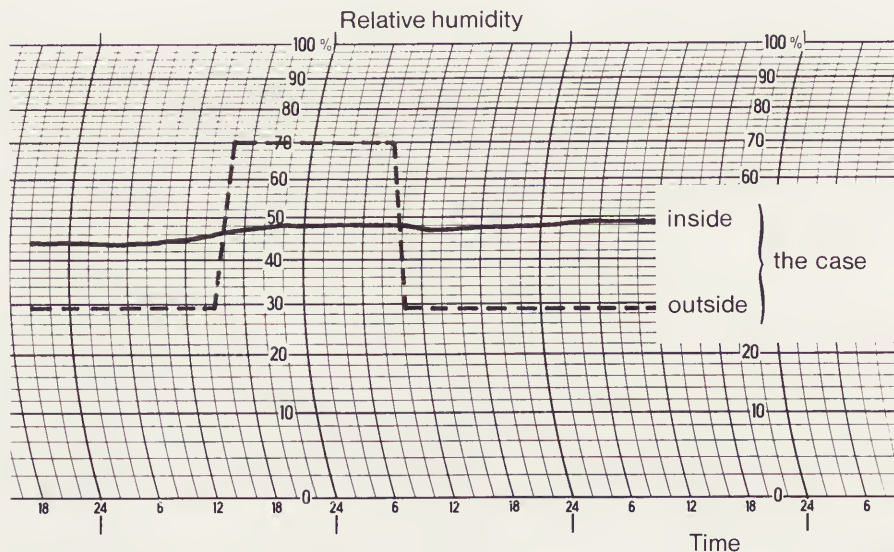
Fig.3 Short time stability

3.2 Long time stability

We observed the long time stability over a period of 30 months (fig. 5). During this time the RH of the air in the office varied from 20 % to 70 %. In the case it remained between 40 % and 58 %. The sharp rise and fall of the RH in the room in autumn and spring corresponds of course to the beginning and end of the heating period. The variations of the RH in the case

4. Conclusions

This limited investigation allows us to answer the three question we were interested in, namely :

1) Does this system actually work ?

The answer is definitely : yes. In the present case we were able to reduce substantially the variation of
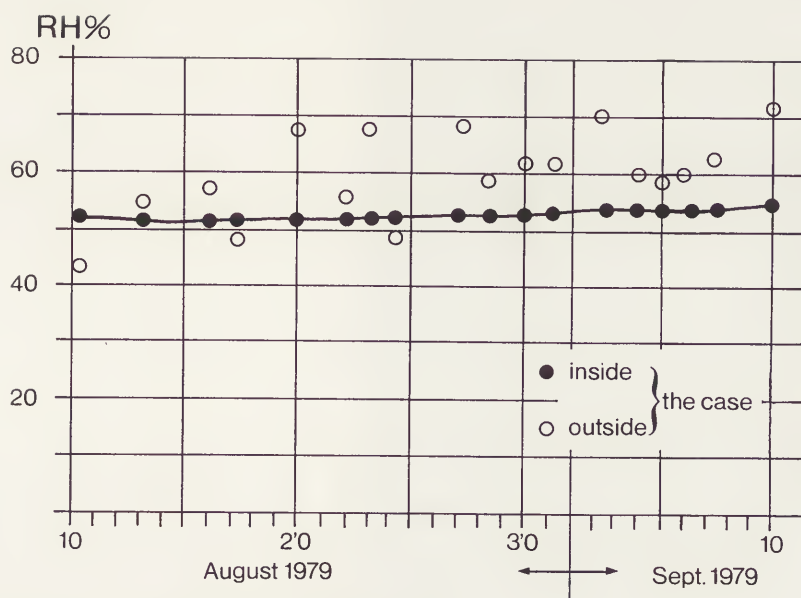
Fig. 4   Stability over one month
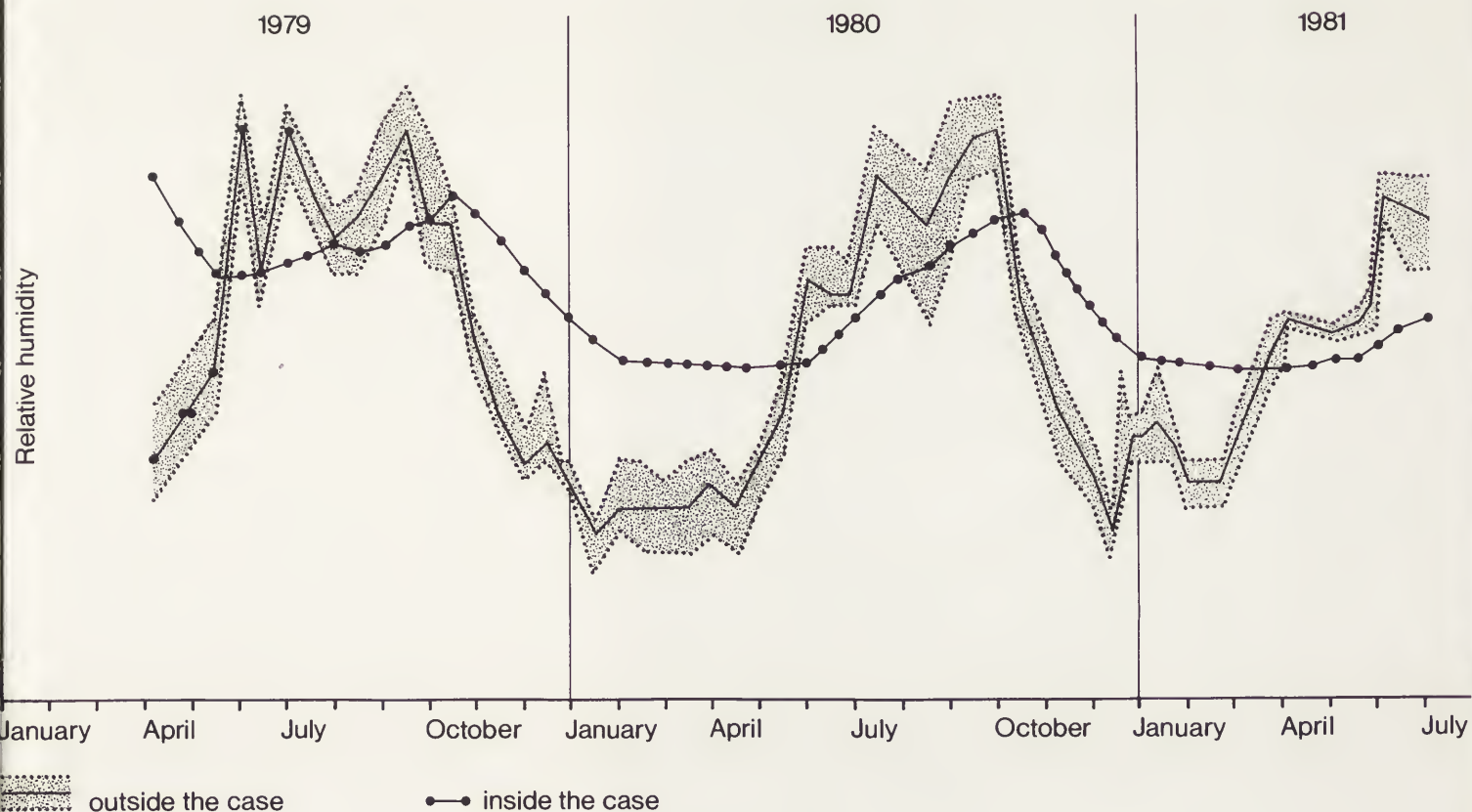
Fig.5   Long time stability

the RH. A wooden object, for example, would not have been exposed to a dangerous humidity level below 40 %, although the RH in the room remained for 3-4 months below 30 %. Daily and monthly variations are completely cancelled out. It is evident that the overall variation of 18 % RH could have been reduced if the case had been better sealed. We were, however, inter-

ested to simulate the conditions of an older museum with simple exhibition cases. As has been shown by others the buffering efficiency of an installation can be improved by the choice of other sorbents than silica gel (4,5).

2) What are the costs ?

The costs of the system are given by the price of the sorbent, in our case by the silica gel. It is not a cheap sorbent, actually it costs in Switzerland 16.-francs per kilogram (7 $/kilogram). For our small experimental case we had to spend 13.- francs (5 $). Following Thomson's advice of 20 kilograms of silica gel per cubic meter air we would expect costs of approximately 320.- francs per cubic meter ($ 140/m3). This may seem rather expensive but it must be kept in mind that the silica gel can be used for many years. This results in very reasonable costs per year.

3) Does the installation need maintenance ?

In our geographical regions, where the RH inside buildings is high in the summer and low in the winter the installation does not need any attendance and can be left for many years. As fig. 5 shows, the curves form 1979 to 1982 are almost identical and the RH remains in the case within acceptable limits. For other regions, where the RH is constantly too high or too low, the silica gel has, of course, to be periodically reconditioned. This can be done with little effort and negligible costs.

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PROBLEMS IN LIGHTING AND DISPLAY: AN EXAMPLE
FROM THE METROPOLITAN MUSEUM

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SUMMARY

The Michael C. Rockefeller Wing of Primitive
Art at the Metropolitan Museum of Art in New
York is an excellent example of how an arch-
itecturally beautiful structure can be dis-
astrous as a museum exhibition area from the
conservation point of view. A large collec-
tion of Oceanic material, all made of light
sensitive organic materials, was to be dis-
played in a gallery one side of which was made
entirely of glass. The ceiling and roof are
also made of glass. The type of glass used is
discussed and the visible and ultraviolet
light readings obtained are given. A trans-
lucent grey screening was installed to cover
the glass which significantly reduced the
visible light levels, but not the ultraviolet.
Further screening in the form of ultraviolet
absorbing film was applied to the glass panes
of the ceiling. While considerable progress
was made in reducing the light levels, the
ideal conditions were not reached. None of
these compromises were necessary had conser-
vation played an active role in the planning
of the wing right from the start.

A recent new wing of the Metropolitan Museum
in New York provides an excellent example of
what can happen in a museum when conservation
does not play an integral role in the policy
making and planning of exhibitions; of how an
architecturally beautiful structure can be-
come a disaster as a museum exhibition area
from the point of view of conservation.

In January 1982, after 13 years of planning,
the Michael C. Rockefeller Memorial Wing of
Primitive Art opened at the Metropolitan
Museum of Art in New York. Art and architec-
ture critics all over the world were lavish in
their praise of the wing, as were authors of
articles in more specialized magazines deal-
ing with primitive art. For the conservators
involved in putting the wing together, the
euphoria was somewhat subdued. A large project
had been completed, but major compromises had
been necessary, compromises that will inevit-
ably prove deleterious to many of the nearly
1800 objects housed in the wing. More impor-
tantly, these compromises need never have been
made had conservation played an active role in
the planning of the wing right from the start.
My purpose in presenting this paper is to pro-
vide an object lesson in hopes that such a
monumental mistake will never be made again.

The wing, comprising 42,000 square feet, opens
off the south end of the main museum building.
Mirroring the wing housing the Temple of Den-
dur on the north side of the museum, its dom-
inant feature is a glass "curtain wall"
sloping upwards from ground level to roof,
some 50 feet. (See figure.) The 7200 square

feet of glass faces due south onto Central
Park. The gallery adjacent to the glass wall
extends the entire length and height of the
wall creating a monumental rectangular space
known as the courtyard. The roof and ceiling
of the courtyard are also of glass.

Housed in the courtyard area is the majority
of the Oceanic material on display in the wing.
It forms the focal point of the wing since it
prominantly displays the Asmat material from
New Guinea collected by Michael Rockefeller
prior to his death on an expedition there in
1961. All of the objects in the courtyard are
made almost exclusively of organic materials:
wood, skin, leather, fur, bark, feathers,
fernwood, reeds and fibers of all kinds. Many
of the objects are extensively painted. From
the conservation standpoint, it couldn't have
been a more unsuitable environment for dis-
playing such objects.

It is hard to believe that such a mistake
could have been made given the vast amounts of
time, energy and money that went into the plan-
ning and execution of the wing. Right from the
beginning more concern seems to have been
shown for the temperature and relative humid-
ity levels of the wing rather than for the
light levels. Although he did express some
concern early on, Nelson Rockefeller, donor of
the collection to the museum, was greatly
taken with the idea of people in the park
being able to view a portion of the collection
through the glass wall.

All but the interior finishing work had been
completed before conservation took an active
role in the wing around 1976. Realizing immed-
iately that lighting was a problem, a system-
atic monitoring of the courtyard area was
undertaken over the course of an entire year.
Readings were taken 3 times a day from eight
different sites within the courtyard. Even
armed with this data, it was not until three
years later (when the author became involved
in the project) that the museum administration
finally admitted that there was a problem. The
visit at our request of Dr. Gary Thomson,
Scientific Officer at the National Gallery in
London, was instrumental in achieving this
change of view.

The panes of glass in the wall are LOF Thermo-
pane Vari-Tran. A reflective silver coating on
the clear glass allows for only 14% trans-
mission of light. This coating was very effic-
ient in cutting down the light as was dramat-
ically obvious when several of the panes were
broken and replaced with regular uncoated
glass. In spite of this, however, walking into
the courtyard from the interior galleries of
the wing was blinding, even on a dull, over-
cast day. Visible light readings ranged from
60 to 1200 footcandles, averaging 550 foot-
candles. As to be expected, the ultraviolet
light levels were equally high, ranging be-
tween 75 and 400 µW/lumen with the average
around 200 µW/lumen. Thomson's recommendation
was not more than 5 footcandles on the organic
and colored materials. It was finally conceded
that something had to be done.

Considerable debate ensued. The designers
jumped at the chance to get rid of the glass
wall altogether for the heavy shadow pattern
projected by its strong window grid proved a
most disturbing, intrusive presence. The
architects, on the other hand, were upset as
they had designed the courtyard area specific-
ally with natural light since the objects to
be displayed there came from cultures that ex-
isted very much in the sun. As well, they were
loath to give up the panorama of the New York
skyline since not long before they had been
forced to give up another trademark feature of

the original plan. A 2000 square foot reflecting pool was built immediately in front of and parallel to the glass wall. Various objects relating to water, canoes, paddles and prows, were to have been mounted directly above it. Eventually, the pool was replaced by a raised platform.

After much debate, a compromise was decided upon. The glass was partially blocked out to cut down on the light levels, but the park and skyline were still visible, although hazily so. Large screens were installed to cover the 11 bays of panes. The screens consist of fiberglas coated with polyvinyl chloride dark grey in color. The medium weave makes them appear translucent when seen from a distance. Each screen is mounted on a motorized roll so that it can be raised or lowered independently of all the others. It was thought by some that the screening would be raised or lowered daily according to the intensity of the sun's rays that particular day.

After the screening was installed in March 1981, extensive readings were taken again of the light levels. The overall visible light had been reduced considerably, the average now being 60 footcandles. The lowest readings (10-15 footcandles) were taken on the platform immediately in front of the screened wall. The farther away one got from the wall, the higher the readings as the ceiling had not been screened. While progress had been made with the visible light, the ultraviolet light levels still remained extremely high. The overall average was 180 µW/lumen while readings as high as 200 µW/lumen were frequently taken.

It was obvious that something had to be done about the glass ceiling to further reduce the ultraviolet light levels. It was made quite clear that it was not permissable to block out any visible light from the ceiling; neither the architects nor the museum administration would make further compromises here. This was partly due to the fact that the uppermost floor of the wing overlooking the courtyard is a separate gallery of 19th century European Art that relies on the sunlit ceiling for illumination.

The glass ceiling, suspended 10 feet from the glass roof, consists of square panes of opaque glass set in a metal grid. Some of these panes have circular holes in them for spotlights. It was decided to cover each of the panes with an ultraviolet absorbing film. Minnesota Mining and Manufacturing's P66 shatter-resistant film was used. Once installed, the ultraviolet light range was reduced drastically to 10-30 µW/lumen, the higher readings coming from the open area farthest from the screened wall.

Although the ideal light levels had not been reached, it was made very clear by the museum administration that no further changes would be permitted. The opening date was rapidly approaching and conservation was forced to accept the light levels as they now stood. It is regretable that such compromises had to be made. It is sadder still in view of the fact that no compromises need have been made at all had conservators been consulted and involved right in the beginning of the planning stages. Only in the later stages did the conservation voice rise above the others, but at a time when it was too late to do anything but compromise. Saddest of all is the fact that it is the objects themselves that will suffer.

Perhaps the worst aspect of all, however, is knowing that in a world renown institution such as the Metropolitan Museum the rest of the museum world is constantly looking at you, taking its lead from what you do and how you do it. What we appear to be saying with the Rockefeller Wing is that daylight is now admissable in museum exhibition space. Of course, the opposite is true. It is fervently to be hoped that there will not be a generation of new, small museums springing up utilizing natural light in exhibition areas. Above all, it is to be hoped that at the Metropolitan Museum and elsewhere conservation will be given an equal voice in the policy making and planning of all aspects of the museum concerned with storage and display. All the frustration of battling the light problems in the Rockefeller Wing will have been worth it if others will gain from our experience.
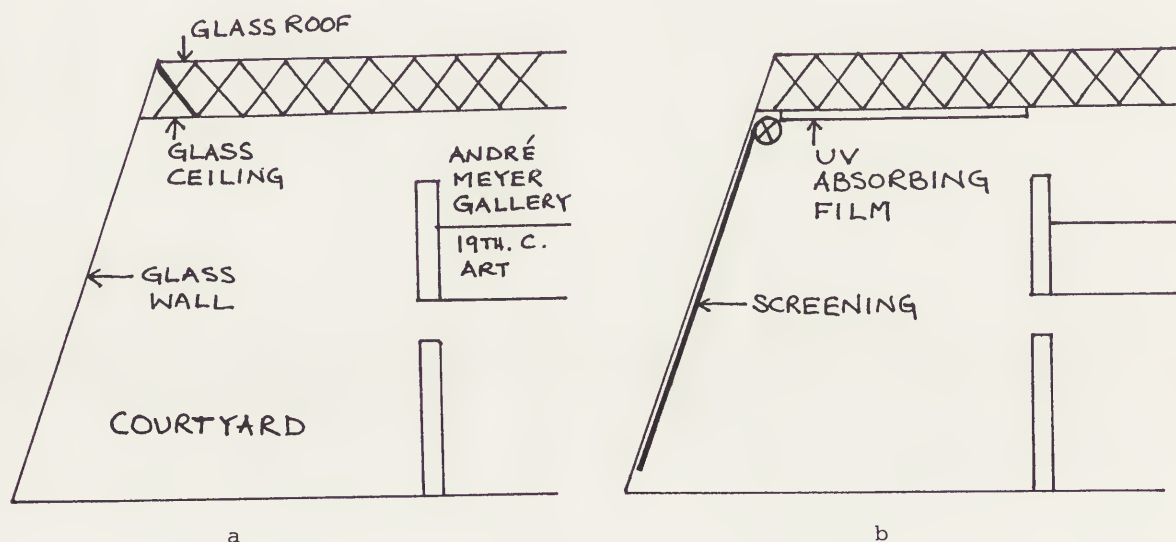
Cross section of courtyard area of Rockefeller Wing, a)before and b)after screening was installed.

TECHNIQUES FOR MINIMISING ENVIRONMENTAL
DAMAGE TO WOODEN OBJECTS MOVED FROM PAPUA NEW
GUINEA TO AUSTRALIA WITH PARTICULAR REFERENCE
TO SEASONING

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SUMMARY

Five large unseasoned wooden artefacts brought
from Papua New Guinea to Sydney needed to be
acclimatised for display within a strict time
limit. The conservation emphasis was placed
on reducing shrinkage and cracking of the
objects by drying them under controlled
relative humidity conditions.

The influence of the drying programme on the
moisture content of the wood and its effect
on shrinkage and fungal activity is discussed.
Other factors affecting and dimensional
stability of wood are also mentioned.

Two main conclusions are drawn: that having
advance knowledge of the drying character-
istics of the species of timber involved is
highly desirably when planning and implement-
ing a seasoning programme for wooden objects;
and that mould growth on wood which has a
high moisture content can be controlled by
circulating sterilized air.

From mid 1980 to mid 1982 The Australian
Museum, Sydney, developed a major new ethno-
graphic gallery based on the life of one
village in the Sepik district of Papua New
Guinea. A very large proportion of the
objects and structures brought back for
inclusion in the exhibition were specially
made for the Museum by the people of Apangai
village. As specially commissioned display
items, these artefacts had to be conserved to
the exhibition opening deadline.

Many hundreds of old and new objects underwent
conservation treatment in preparation for the
exhibition. Of these, five very large painted
wooden objects, newly carved from freshly-
felled trees, were amongst the main conserv-
ation problems. Their high moisture content
was expected to give rise to biological
activity, dimensional changes and damage to
surface decoration, during their period of
stabilisation to different climatic conditions.

It is the behaviour and treatment of these
objects in relation to moisture and relative
humidity (RH) which will be covered in this
paper.

CLIMATE

All field work at Apangai was scheduled for
the "dry" winter season, but because of the
tropical locality, some precautions were taken
against the possibility of wet and humid
weather.

The two month so called "dry" period during
which the field work was going on, in fact
turned out to be phenomenally wet and humid.
It rained nearly every day, the RH where the
objects were kept stayed in the high 90's and

the storage areas were dark and frequently
flooded. Since these conditions were consider-
ably more extreme than had been expected, a
more detailed appraisal of the climate of the
Pacific region was undertaken after the return
of the expedition and yielded interesting
information. The term "dry" used in this
climatic zone bears no relationship to monsoon-
al weather patterns. The climatic belt in
which Apangai is situated, ($3^{\circ}40S$, $143^{\circ}E$) is
identified by Trewartha (1968) as having an
"Ar" type climate. This is described as a
Tropical Wet and classified as having from ten
to twelve months of the year which are wet and
up to two months in which less rain may fall.
From meteorological data obtained for the
region it was found that Apangai has what is
known as a moderate average annual rainfall of
approximately 2000mm, apparently evenly dis-
tributed. There is in fact, no easily identif-
ied "dry" period in this area.

THE PROBLEMS

The objects were carved from rainforest hard-
woods which had an estimated moisture content
(m.c.) of between 100 and 180% (i.e. 100-180
parts of water to each 100 parts of dried
woody material). Before more was known about
these timbers it was thought desirable that
they should be air-dried to an equilibrium
moisture content (e.m.c.) of approximately
11-12% within a period determined by the pre-
set gallery opening date. This period,
initially planned for nine months, was
progressively extended to eighteen months.

The acclimatisation of green timber from a wet
tropical area to a stable condition in the
very different climate of Sydney, involved
conflicts between mould growth and possible
rot, the humidity requirements for careful
seasoning, the completion deadline and the
dimensional changes to timber that occur with
rapid loss of moisture.

The problems encountered throughout this
project were inevitably closely related; the
corrective treatment applied to one problem
was frequently the cause of another. This
paper, however, will discuss seasoning and
fungal problems separately. Insect control
and many other conservation aspects of the
project will not be dealt with.

PLANS FOR DRYING THE GREEN WOOD CARVINGS

Five wooden carvings up to 3 m in length and
0.5 m in diameter were unwrapped after arrival
in Sydney. All were thought to be in sound
condition and relatively free of cracks,
although it was later surmised that one of the
carvings had been badly affected by rot down
the central core of the wood where a natural
fork in the trunk had occurred.

The carvings were made from different woods.
Three were carved from a species of Gmelina,
probably G. moluccana and one of the other two,
a female figure, from a species of Celtis.
The fifth carving was not positively identif-
ied and will be referred to as the 'Lintel'.
Gmelina is described by Bootle (1971) as an
extremely slow drying wood. It is also
extremely durable, has low shrinkage character-
istics and, once dry, remains very stable.
Celtis on the other hand, is described as a
wood of low durability which was borne out by
the extensive rot that earlier affected the
female figure, and demonstrated far greater
susceptibility to mould than the Gmelina
carvings. It also has relatively low shrink-
age characteristics.

Fig. 1.   Female figure freshly carved from <u>Celtis</u> timber,   Photograph by J.J. Freeman
          being carried downriver to Apangai for painting

The carvings had been surfaced with a ground of finely divided river clay, then painted with local mineral pigments, charcoal and 'battery black' in a thin dispersion of polyvinyl acetate. The pigments, although requiring attention, were not given a high conservation priority at this stage as they were to be restored, if necessary, by the Apangai artists after the wood had achieved dimensional stability.

A drying schedule was drawn up, based on the need to stabilise the carvings to progressively lower RH conditions until reaching the expected mean RH for the gallery at the time of the exhibitions opening. Projected RH values for this period were based on an analysis of the last ten years' meteorological data. The major part of this planning was undertaken in co-operation with the Wood Technology Division of the N.S.W. Forestry Commission.

CONTROL OF RH

One of the secondary objectives of this project was to undertake as much of the work as possible using simple, cheap and practical methods so that the successful aspects of the project could be passed on to other organisations operating with smaller budgets and manpower resources, particularly in the Pacific region.

To maintain controlled RH conditions over a long period of time without the use of air conditioned premises, a large indoors plastic chamber or "tent" was constructed to fit over the wooden carvings out of a cheap grade of polythene film secured with P.V.C. tape over wooden battens. The wooden floor was also covered with polythene. A window of clear polyester film was incorporated to give good viewing access to the objects and thermohygrograph and so minimise the need for access inside the tent, thus reducing the amount of air exchange. A simple polythene flap door was also included, with a strip of hook and pile fastener (Velcro) to act as the sealing device. Windows near the tent were covered with reflective foil to reduce temperature variations.

Initially, the desired very high RH was maintained in the environmental tent by spraying water onto towels strung along clotheslines. The number of towels, degree of saturation and frequency of water application was determined by the external temperature conditions, the surface area and moisture condition of the wood and air leakage from the polythene tent.

This method of controlling the RH appeared satisfactory at the beginning of the project, when the temperature was around 13-21°C. When the temperature started to rise in late Spring and early Summer, it became quite inadequate. There was not sufficient manpower to maintain spraying routines at night and at weekends. Unfortunately, these unscheduled drops in RH, while retarding mould growth, may have been responsible for premature initiation of cracks. By the end of the third month this method of humidification, while extraordinarily cheap, had to be abandoned. It was replaced by a

domestic steamer with an 8 litre capacity and a variable evaporation rate of 0.4-1.0 litres per hour.

During the early part of the summer a constant output of steam maintained the 80-90% RH required during the day. At night, even though the water supply became exhausted, the combination of the lower temperature, the high RH buildup during the day and the loss of moisture from the high volume of wood in respect to air volume, maintained a reasonable twenty-four hour RH gradient so long as external conditions remained fairly constant. Throughout the period in which the steamer was used, no difference in temperature was detected between the inside and outside of the tent. At times however, unseasonal drops in temperature or rises in humidity resulted in an excessive buildup of moisture in the tent leading to condensation, and accordingly a further modification had to be made to the system.

Because of this difficulty of adjusting the RH to compensate for ambient extremes, a small portable humidity controller (Humidistat) was assembled to activate the steamer. It operated off a 12 volt direct current because of the potential hazards of high voltages in such a humid atmosphere. The remote sensor was attached to the wall of the tent and was able to control the RH to within $\pm$ 5% of the pre-set level.

This final adjustment to the system, while adding a level of technology not originally intended for the project, enabled water to be added to the atmosphere at critical times when staff were not available. It was further noted that the 8 litre steamer reservoir, when triggered by the humidity controller was adequate for the 6.5 m^3 tent space in the prevailing climatic conditions. In fact, probably because of the large volume of buffering material, the controller was only activating the steamer at a maximum rate of twice in each twenty-four hour period. This method provided reliable environmental conditions until such time as humidity needed to be removed from the atmosphere. At this stage a small refrigerant-condenser type dehumidifier was placed in the tent and kept there during the period that RH was expected to rise above the level determined for the seasoning schedule.

The need for dehumidifying equipment had not previously been envisaged, as the whole drying process was originally due for completion in a season of low humidity. In fact, the programme was extended into a second Summer, a time of high humidity.

To assess the response of the wood to RH conditions, a programme of monitoring the moisture content and the crack development of the objects was implemented. The moisture content measurements were carried out using a resistance meter with a sliding hammer electrode.

All the carvings were being treated and it became apparent during monitoring that the two groups of objects, the Gmelina carvings and the others were drying very differently. There was accordingly no possibility of establishing a schedule that would result in a safe route to the equilibrium moisture content required for both groups within the designated time scale. In practice, the drying schedule was continually modified as the moisture content and its affect on cracking was assessed.

RH MONITORING

Environmental monitoring was first carried out using an electronic unit with a remote sensor placed inside the tent and a normal thermohygrograph outside to compare information. Calibration of the two instruments was checked daily with a sling psychrometer. The electronic device (Rustrak) was used because it incorporated a remote sensor which could be stationed inside the tent with the chart recorder kept outside during the early monitoring period when conditions of high humidity or condensation could have affected the ink and paper of a conventional thermohygrograph. This type of equipment is not, however, very accurate at high humidity and was replaced with another thermohygrograph as soon as the RH was brought below 90%. The weekly RH mode was calculated from the charts and plotted with the crack measurements for the corresponding period.

AIR DRYING THE WOOD CARVINGS

The removal of two sorts of water is involved in drying green wood. Free moisture in cell cavities is first removed followed by removal of bound water saturating the fibres of the cell walls. It is removal of this bound moisture which can lead to stress and then shrinkage if it is removed too quickly which results in too steep a moisture gradient between the surface and the centre of the wood.

From the time of manufacture of the artefacts in Papua New Guinea to the time the seasoning schedule began in Sydney was four months. Two of these months passed in Papua New Guinea where the timber would have started to dry. A considerable loss of free moisture would have taken place there, although a still very high moisture content would have been preserved in the sealed packaging during transport. The loss continued in Sydney although possibly at a slightly reduced level under cooler conditions and approximately 90% RH provided in the environmantal tent.

Moisture content readings on the surface of objects (up to a depth of 6mm) after a further two months indicated a moisture content in excess of 35%, or well above the fibre saturation point (25-30%). The objects were then accordingly left at 90-95% RH to continue the gradual process of losing free water until the fibre saturation point threshold was reached at the surface of the objects. At this stage accurate moisture content readings could begin to be taken. Above the fibre saturation point the moisture content of wood cannot be accurately measured.

Significant measurements were not obtained until four months after the seasoning schedule was underway when values as low as 24% were obtained on the surface of the faster drying objects, the female Celtis figure and the 'Lintel'. Moisture content readings were then taken approximately every two months at 3 mm intervals up to a depth of 25 mm. Differences in drying behaviour among the various items soon became apparent and towards the end of the drying schedule a division was made in the tent so that two different levels of RH could be maintained for the two groups of wood drying at different rates. The faster drying carvings were kept at a 5% higher RH than the slower and apparently more stable Gmelina carvings. Subsequent analysis of moisture content data indicated that the two faster drying objects reached fibre saturation point throught their thicness within seven to twelve months of the start of the programme. They then continued to season, with their moisture gradients becoming progressively more level until they were placed in the gallery at an
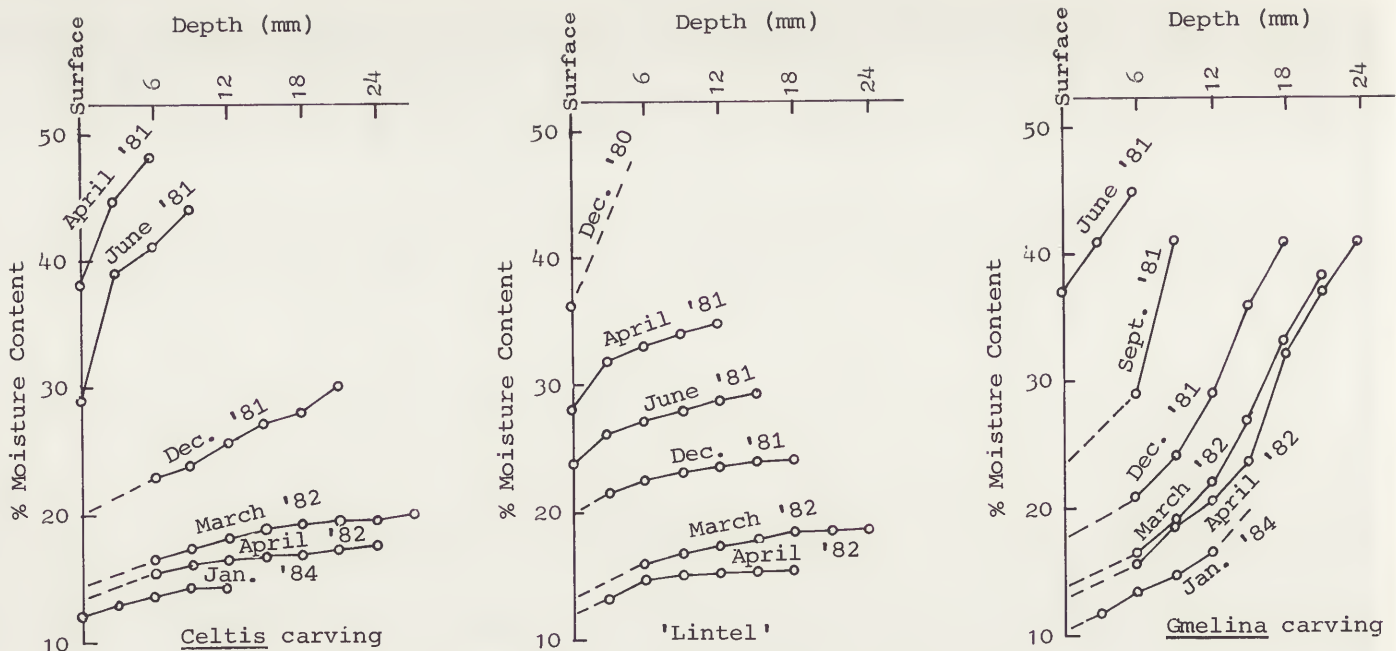
Fig. 2. MOISTURE GRADIENTS OF THREE OBJECTS DURING DRYING

average moisture content of 15%, eighteen months after the beginning of the seasoning programme. The Gmelina objects however, proved highly resistant to drying, and although at the time of being placed in the gallery they had an average surface moisture content of 15%, it is believed that only the outermost 20 mm had dried to fibre saturation point or below.

Early in the project the end-grain of the wood carvings was covered as much as possible so as to reduce unnecessarily fast and localised escape of moisture. This could not be achieved on the 'Lintel' because of the deep and complex nature of its carving which may, in turn, be one of the main reasons why this object cracked much more severely than the others. Throughout the project it was the ongoing assessment of crack development which provided the main guide to seasoning requirements.

CRACK MONITORING

As cracks started to develop fairly early in the seasoning schedule, well before the fibre saturation point was reached, a measuring programme was set up in an attempt to plot the behaviour of the carvings. Changes in the size of the first cracks to appear in the objects were monitored throughout the project; their widths were measured and graphed up on a weekly basis together with RH data.

Except in one instance, the cracking was not very severe and responded well to alterations in RH. The exception was the heavily carved 'Lintel' with extensive exposed endgrain providing a high surface area for evaporation. Generally it is believed that cracking of this type of carving is inevitable if a time limit is placed on its seasoning or it is left to dry in an uncontrolled environment.

As it was necessary to place all of the carvings on display before equilibrium moisture content had been reached, monitoring of cracks and moisture content was continued, although only sporadically as this necessitated partial dismantling of the exhibition. Measurements taken over twentyone months after the objects
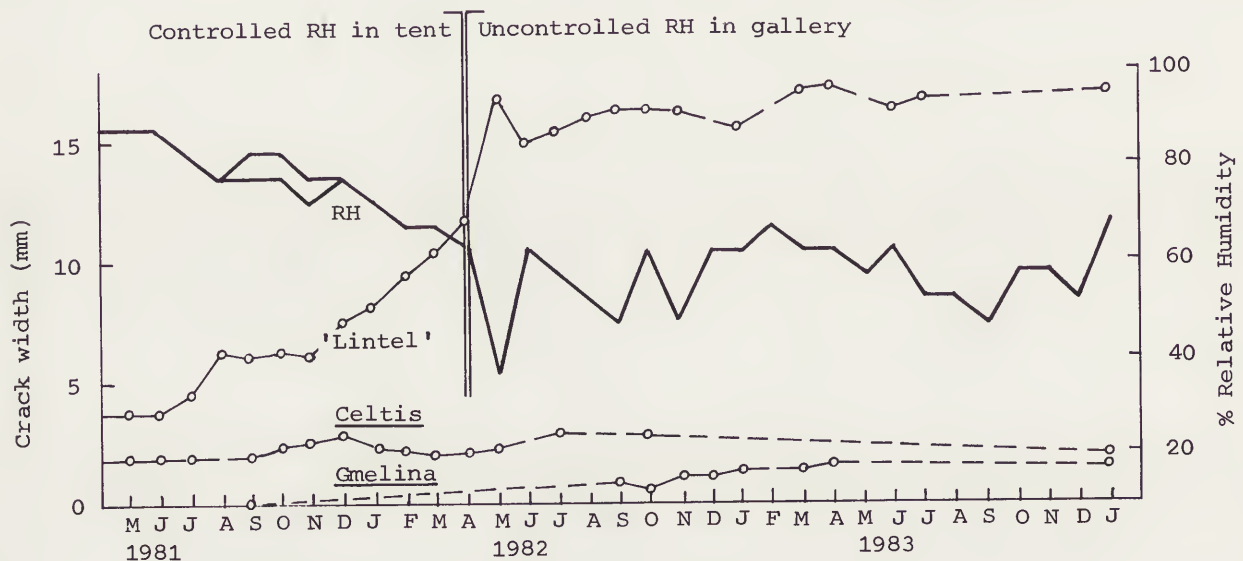
Fig. 3. RELATIONSHIP OF CRACK GROWTH TO RELATIVE HUMIDITY

were installed in the gallery showed no increase in crack width for the well dried objects which had now reached equilibrium moisture content. In fact the cracks on the Celtis objects had actually closed a little. For the three Gmelina objects, however, which showed only surface drying and were still above fibre saturation point 30 mm from the surface, cracks had very slightly increased.

FUNGAL ACTIVITY

There was extremely marked fungal activity on the surface of all the artefacts throughout their manufacture and use in the village Spirit House and up to the latter part of their conservation treatment in Sydney.

In the village, surface moulds started to develop immediately the carving was completed on the fresh timber, and continued to colonise the river clay and multiple layers of mineral pigments applied to the surfaces despite applications of thymol (sprayed in a solution of ethanol or vodka, depending upon supply availability). It was not possible to utilise the properties of more effective or residual fungicides because of the likely health hazard: people were in constant physical contact with the carvings while they were being prepared and poor air circulation prevailed in the closed-off holding area. It was also not possible to use the sun as a sterilizing agent on the opaque painted surfaces either, because of the totally secret and sacred nature of the artefacts, which had to be hidden from uninitiated people at all times.

After the final application of the surface paint decorations and thymol, the development of further disfiguring mycelia was temporarily arrested. Following the ceremonial use of the carvings by the village people, they were packaged in several layers of acid-free tissue paper, polythene bubble plastic and reinforced cardboard crates tightly packed into shipping containers.

On arrival in Sydney the Museum containers were fumigated with methyl bromide according to quarantine requirements.

All of the objects were unwrapped in the laboratory with considerable trepidation. The painted wood, while still in a semi-green state, had not only been sealed to prevent uncontrolled moisture loss on the voyage, but had also languished for seven weeks, strike-bound in metal containers on the wharves of the tropical port of Wewak on the North Coast of Papua New Guinea. Rot, mould and displacement of pigment were all anticipated possibilities. However, despite the extreme wetness of the objects and internal wrappings, the pigment was in good condition and there was no visible evidence of fungal activity. One disaster did, however, occur - the total disintegration of the tissue paper under the wet conditions. The paper was now clinging to the surface of the wet objects in tiny pieces which required a huge outlay of man hours to remove, as well as being the cause of damage to the painted surfaces.

When the carvings were first unwrapped in Sydney, no mould was visible on the Gmelina carvings and only minor spots on the 'Lintel' and Celtis carvings. These were immediately covered in thin (12.5μ) polythene which allows access of ethylene oxide vapour under pressure, and fumigated using a 10/90 concentration of ethylene oxide in carbon dioxide, and maintained at 165-193 Kpa for twenty-four hours. This was undertaken mainly as a precaution against insect borers. All objects were then placed in the tent in

an atmosphere of approximately 95% RH. Three of the objects were uncovered and two of them left wrapped in the thin polythene film.

The decision to subject the painted carvings to such high humidity was done in the knowledge that this might promote fungal activity but that this could either be controlled or, if necessary, surface discolouration could be restored by village painters. Two of these men who had carved and painted the objects at Apangai were coming to Sydney to help with the project.

After approximately one week at this high humidity, a virulent floral growth had developed on all of the upper surfaces of the objects that had been unwrapped and that were now exposed to the atmosphere inside the tent. The Celtis carving was by far the most seriously affected, with what appeared to be a complex range of micro-fauna growing to a height of up to 3 cm. All of the objects were supported at a slight angle to the vertical providing a better catchment for fungal spores on the upper, rather than the under surfaces. Species from nine genera of moulds were identified with fourteen species of Penicillium representing the dominant genus. In addition, a wide range of yeasts and bacteria were present.

At this stage a number of ideas were mooted as to why there was no fungal growth on the objects while they were wrapped up, followed by such an epidemic explosion of mycelia once they were exposed to the atmosphere. The discussions covered the possibilities that the supply of oxygen available after the objects were sealed was too limited for germination and growth of normally present aerobic mould spores; that there was a total absence of light during this period; and the possibility that access of mould spores onto the objects was prevented by their wrappings and that germination of previous spores may have been inhibited by earlier applications of thymol, or the continued slow release of ethylene oxide. No serious attempt was made to find the answer and so no conclusions can be offered.

In addition to the surface moulds, active rot was suspected within the core of the Celtis carving. Samples were taken and repeated attempts were made to isolate the organism responsible. While samples were being drilled for, it was found that a major section in the centre of the object was hollow. This fact, together with the fact that it had not been possible to isolate any rot fungi, indicated a strong possibility that the rot had occurred at a much earlier stage, when the tree was growing. This was the only evidence of rot found throughout the project. As an emergency procaution however, while an attempt was being made to culture and isolate the suspected rot fungi, the Celtis carving was fumigated using methyl bromide as it was too large for our ethylene oxide chamber. A follow-up treatment was also administered to provide residual protection against rot while the environmental humidity was still dangerously high. A number of small bore holes, 6 x 90 mm were made in the spongy wood area and filled with boric acid. Their number and location in the wood was such that, with the anticipated rate of diffusion through these very porous areas, all the affected wood would be protected.

MOULD CONTROL

During the first severe outbreaks of mould in Sydney, the objects were repeatedly sprayed with a 2% solution of sodium pentachlorophenol in ethyl alcohol. After four applications of fungicide within the first three and a half

months of the project, this process of control was reviewed. Although the tent and the area in which the tent was located were entered only by conservators wearing fully protective apparel, it was considered (because of the toxicity risks involved, the possible buildup of phenolic compounds on the surface of the objects and the probability of pigment discolouration) that this method of control would have to be abandoned. Instead, germ-icidal ultra violet fluorescent tubes (GE G30T8) were used. These were attached to the timber framework supporting the plastic-sheet ceiling of the tent. The objects were shifted away from close exposure to the radiation. Although the pigment minerals identified on the surface of the objects were extremely inert and provided an opaque barrier to the underlying wood, further tests on these were carried out. Samples of all the paints were subjected to accelerated aging tests which confirmed their stability.

A small domestic oscillating fan was installed at the bottom of the tent to ensure good air movement through the path of the sterilizing radiation. It was decided, somewhat arbitrarily, that the UV lights should be operated twice a day for a period of one hour. The system was activated automatically by a time switch. About two weeks after this system had been running, however, the smell of ozone was detected. Reduction of UV time to one hour per day appeared immediately to correct the problem.

To look at the effects of the UV tubes, an air spora count was undertaken inside and outside the tent and the results were compared. Analysis of the two groups of cultures indicated that UV irradiation had had no effect on the numbers of spores within the tent which remained comparable to outside, but that the germination rate of those inside the tent was severely retarded.
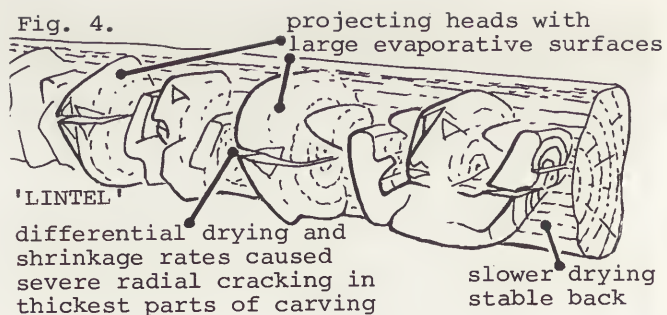
Four weeks after the UV had been operating and the RH was still in the 80-85% range, minor mould spots were found mainly on the protected under surfaces of the objects. These were lightly cleaned off using ethanol swabs. They did not reappear. No further methods of treatment against mould needed to be carried out before the UV tubes were re-moved from the tent when the RH was lowered to 65%. At this point, surface moisture had dropped below the level required for even the most xerophilic fungi. The decision to leave the UV running until this relatively low RH was reached was based on the work of Pitt (1975) and Casey, on the potential for mould growth under low moisture conditions.

Subsequent inspection of the objects in the gallery situation showed no mould growth, as was to be expected with surface moisture content readings at 15% or below, in spite of their high internal moisture content. As the carvings were on open display rather than in sealed showcases, there was no opportunity for a high RH buildup to be caused by ongoing evaporation of moisture from the objects.

CONCLUSIONS

Our attempts to season large wood carvings within a strict time limitation through control of RH, pointed out the need for early timber identification. For most timbers, the drying, shrinking and durability character-istics are known, at least to the genus level: having had this information from the outset of the project would have been invaluable.

In the project described, it is now apparent that there were three distinct classes of objects being treated simultaneously:

Fig. 4.

projecting heads with large evaporative surfaces

'LINTEL'

differential drying and shrinkage rates caused severe radial cracking in thickest parts of carving

slower drying stable back

First were the carvings made from Gmelina sp. which is extremely resistant to drying. In fact, on open display this timber has behaved very satisfactorily when only surface dried, with little evidence of cracking. The drying programme has had little effect on these items.

Secondly, the Celtis sp. responded well to the drying programme. It should be noted that this object had been simply and not too deeply carved.

Thirdly, the 'Lintel' must be considered separately. It was very heavily carved from one face only, exposing large end-grain evaporative surfaces on one side of the piece and long, uninterrupted longitudinal grain on the other. With the same drying character-istics as the Celtis carving severe cracking was nevertheless inevitable when seasoned to a time limit. To minimise cracking of this piece would have required extremely slow and controlled drying with no constraints of the 'Lintel' cracking, some carving away of the excess wood behind the very thick sections would have established additional surfaces of evaporation in the opposite direction and helped to reduce the moisture gradient and consequent stress to the wood. The large rot cavity in the Celtis carving, probably contributed to its more even drying with less cracking.

Important considerations when drying wooden objects by means of controlling RH thus include:

*Identification of the timber used and knowledge of its drying, shrinking and biodeterioration characteristics.

*Assessment of likely departures from normal behaviour due to the special history of the wood or the forms imposed by the carvers.

*Assessment of relative size and mass of individual objects, which will affect drying rates.

These considerations should form a basis for sorting objects into groups requiring separate treatments.

The packaging methods used were very satis-factory, although one of the materials used was not. Whilst a large amount of absorbent material was needed to help buffer the moisture problems, a material with a proven wet strength should be substituted for the tissue paper. The Gmelina carvings might have benefitted from packing in a material more porous than the polythene bubble plastic, to allow gradual drying to proceed during the period of trans-port. However, the gain of a few weeks drying for such a slow drying timber may not have been very significant.

With regard to maintaining conditions in the environmental tent, automatic monitoring and control of RH was found to be essential when using such devices as a steamer and small dehumidifier.

The use of standard chemicals to control
mould growth under conditions of high moisture
content was largely unsatisfactory. The UV
sterilizing system, however, was found to be
exceedingly successful. It was used for a
sufficient time when the surface moisture
content of the timber would have otherwise
supported vigorous mould growth, to prove its
effectiveness.

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ACKNOWLEDGEMENTS

Section 18

Conservation of Leathercraft
and Related Objects

Conservation des cuirs
artisanaux et objets similaires

CONSERVATION OF LEATHERCRAFT AND RELATED
OBJECTS

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            Mr. Z. Szalay (Hungary)
            Mr. W. Schmitzer (W.Germany)

Programme 1981 - 1984

1. To promote responsible conservation of
   leathercraft products and artistic and
   archaeological objects of leather as well
   as other objects through communication
   among the members.

2. To encourage the exchange of experimental
   findings or other relevant information
   providing this does not interfere with
   the sovereignity of a particular work
   or with the priority reserved for the
   publishing of this finding.

3. To examine the merits of available methods
   and to develop new ones in matters con-
   cerning the salvage of dray, pulverising
   archaeological leather decay, in particu-
   lar the red rot.

4. To study the conditioning of leatherwork
   with respect to exposition and storage.

5. To refine the composition on leather
   dressings employed in the treatment
   of decaying leather.

6. To assess existing training programmes
   and to stimulate their development by
   propagating themas as well as by trans-
   lating the instructions on which they
   are based into various languages.

WORKING GROUP: CONSERVATION OF LEATHERCRAFT
AND RELATED OBJECTS

An overview on activities.

Coordinator: T. Stambolov, Central Research
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Considering that the second part of the title
of this working group, that is, non-leather,
has so far, been neglected, it is now deemed
proper as a compensation, to present an out-
look on some of the as yet unheeded materials.

An investigation provoked by a message (A.
Carter: "People as pictures" New Society,
8 October 1970 pp. 636-7) that "in Tokyo there
is a private museum devoted to the display
of particularly fine specimens of tattooed
human skins", and conducted throughout a de-
cenium revealed, recently, some intriguing
details:

While the tattooing technique might have
accidentally resulted from the primitive me-
dical pratice of rubbing soot into wounds, it
is, since the Fedual Period a well-established
tradition in Japan. It is based on the absorp-
tion of pigments through the capillaries
pierced into the skin with two or more needles
tied in a bunch. For Black-and-white tattoos
charcoal ink (sumi) was used, which once under
the skin, turned into an indigo or deep-blue
color. Beside black, also brown, vermillion
and white pigments were employed in tattooing
and these colours formed the tattooing palette
of the pre-World-War II days. The white tat-
too (Ashiroi-bori) deserves a special
mentioning here -a rare form of tattoo-, as it
is invisible to the naked eye and emerges only
when one bathes or becomes slightly intoxica-
ted. The easiest way to comprehend tattooing
is to see it in terms of social distinction.

Tattooing for punishment, and also as a sub-
stitute for punishment, due to criminal offen-
ses is called irezumi. And tatooing for adorn-
ment is know as horimono or gaman. In this
tattooing style the body decoration starts on
the back and stops at the elbows because such
distribution reflects refinement of spirit
and higher-ranked occupation. It patterns
the skin with the designs of famous woodblock
artists and the process of tattooing is on the
whole extremely painful. The sufferance there-
by is, therefore considarble as the tattooing
may take as long as a year of weekly visits to
a tattooist before the work of art is complete.
It is assumed that masterpieces of the same
order as the woodblock prints are at display
now at the aforementioned museum (Medical Mu-
seum, Medical Department, Tokyo University,
3-1 Hongo 7-Chome. Bunkyo-Ku, Tokyo, Japan).
The collection of the museum amounts to more
than 100 tatooed skins and they have been pre-
pared for display as follows:

1. Separation of the skin from the corpse.
2. Immersion in formalin for about 6 months.
3. Removal of the subcutaneous fatty and con-
   nective tissues.
4. Immersion of the actual ink-decorated skin
   in formalin for 6 more months.
5. Very slow drying in a shaded space.
6. Display in conditioned and controled en-

vironment.
The definite preparation of a tattooed skin
takes about 2 years. For further information
concerning in particular the conservation of
tattooed skins, one may contact Mr. Jutaka
Yoshido at the above address.

Another related matter with respect to leather
i.e. ivory, is discussed by Michel Doussy in a
quite original way in his "The Art of
Restoring Antiques", Times Books, London 1978.
From this French source the following appears
unfamiliar and hence of interest for the pre-
sent review: The ivory used by sculptors and
craftsmen in both Europe and Asia, comes al-
most invariably from Africa. It falls into
two classes: hard ivory is produced by ele-
phants whose lives have been spent in humid
environments (Guinea, Gabon and the Congo). It
is heavy, has no grains, no vein-like markings
and its colour is a fine roseate white which
turns whiter still with age. It is used by
sculptors, miniature painters and toymakers.
On the other hand soft ivory is yielded by
elephants in dry climate (Ethiopia, Egypt
and Zanzibar). It is tender and resilient and
because of these properties, it is mainly used
for the manufacture of billiard balls and pia-
no keys. Broken pieces of ivory can be glued
together with the same adhesives are especial-
ly suitable as they do not stain ivory. If the
pieces to be glued are of insufficient thick-
ness, a delicate little dowels modelled from
scrap ivory, must be inserted into holes bored
in the broken fragments. However pinning of
this kind can be omitted if the adhesive used
is the very strong epoxy resin. But if the
fracture is of such a magnitute that a pinning
bond is thought undispensable, the holes bored
in the ivory are filled with epoxy resin and
the resin is then reinforced with a few fibres
taken from a glass fibre cloth.

One more related matter, namely feathers, and
specifically their conservation, their selec-
tion for the purpose of decoration and garments
and the techniques employed in the making of
feather cloaks, caps, bonnets and collars, are
exhaustevely described by Karen Stemann Peter-
sen and Anne Sommer-Larsen in their article:
"Techniques Applied to Some Feather Garments
from the Tupinamba Indians, Brazil" in Folk,
vol. 21-22, 1979/80 pp. 273-270. Feathers were
also the subject of the lecture that Mrs. J.M.
Adriaans-Buij delivered at the meeting on
"Leather, Furriery, Feathers in Garments and
headdress"(November 18, 1982 in Arnhem, The
Netherlands). In it the history of the use of
feathers, as well as the social significance
associated with the kind of feathers employed
and the position of the feathers on the body
wearing them, were put in a very balanced per-
spective. In addition other lecturers at the
same meeting gave a note worthy presentation
of the principles in cleaning and conservation
of garments made of leather and/or furs.The
meeting was organized by the Dutch Textile
Commission and the proceedings (in Dutch or
German) of the meeting,which are forthcoming
at the time of this writing, may be ordered at
the following address:
Commission for the care of museum textile
legacy, Minister Loudonlaan 57,
7521 BB Enschede / The Netherlands.

MASS RECONSERVATION OF ARCHAEOLOGICAL LEATHER: A CASE STUDY

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SUMMARY

The contamination due to extensive fungal growth of an excess of 10,000 items of previously-conserved archaeological leather initiated a research project to investigate, evaluate, and compare methods of reconservation. Previous conservation mediums were based on British Museum Leather Dressing or lanolin. Solvent extraction of the old mediums with petroleum spirit 60° to 80°C, white spirit, and Genklene (stabilised 1,1,1-trichloroethane) were examined. Impregnation of Genklene-extracted leather with polyethyleneglycol (PEG) 400, glycerol, sorbitol, and PEG/glycerol combinations in ethanol were investigated. The quantity of finds requiring treatment imposed restrictions on the method of treatment selected as well as its execution. The affected leather was mechanically cleaned, extracted with Genklene, and impregnated with 10%/10% PEG/glycerol v/v/v in ethanol. The treatment was carried out on a large scale with consistent and acceptable results which continue to be monitored on a periodic basis.

INTRODUCTION

With the advent of large-scale excavations in the urban areas of Northern Europe came the need for methods and materials with which to conserve vast quantities of recovered wet archaeological finds. In particular, this need has focused on waterlogged wood; however, other organic materials such as leather, textiles, bone, and shale have demanded attention as well. As for wood, many materials and techniques have been investigated. Concerning leather, the surveys by Stambolov [1], Carlsson [2], and Jamieson [3] reveal the wide range in number and quantity of treatments used presently and/or in the past. Investigations by Ganiaris et al. [4], Carlsson [2], Sturge [5], and Payton [6] have attempted a critical evaluation of reported treatments in use. Repeatedly, the question of reversibility arrises - are the materials removable with time. Most answers are theoretical and speculative and reported attempts are not plentiful. The present work describes one case study of the removal of old conservation mediums from and the reconservation of archaeological leather.

CASE HISTORY

Background

Excavations of the mediaeval levels in Norway are the responsibility of Riksantikvaren, a government agency within the Ministry of Environment. The post-excavation handling (conservation, storage) of recovered finds is the responsibility of the five regional museums which are funded by the Ministry of Cultural and Scientific Affairs. During the early years of large-scale excavations undertaken by Riksantikvaren there was little or no planning and coordination of resources and funding to properly accommodate post-excavation needs. The present case history is, in part, a result of this policy.

Riksantikvaren began large-scale excavations of the mediaeval levels in the City of Trondheim in 1970. Prior to 1974 most finds were treated on-site by excavating personnel. Beginning in 1974 finds were processed at the Conservation Laboratory of the University of Trondheim, Museum but returned to Riksantikvaren for post-excavation study and storage.

Prior to the completion of the Museum's new climate controlled storage facilities in 1982, the storage of all finds from the City's excavations was overseen by Riksantikvaren. Storage facilities consisted of acquired space in old buildings scattered around the city. These facilities not only had no provisions for climate control but were rarely monitored. Although situated relatively far north geographically, Trondheim's climate fluctuates between coastal and continental. This results in moderately cold, dry winters and cold, wet summers.

Considering these factors - inadequate conservation, unmonitored, unregulated storage, and wet summers - the preservation of excavated material was endangered. Most of the leather finds excavated between 1970-74 were stored together. The outbreak of fungal growth on some leather items in 1975 could not have been unanticipated. This leather was reconserved in 1976. In 1977 it was discovered that the remaining leather items had been subjected to dense and prolonged fungal growth and insect infestation. Almost 2,000 registration numbers comprising an excess of 10,000 items totalling 150 kg. were affected. These items were removed to commercial freezers at the City's harbour where they remained at -40°C for several years.

Description and Condition

The leather items, presumably vegetable tanned, date from the Middle Ages (1050-1536). A wide range of items are represented but the majority of pieces are offcuts or associated with shoes. Throughout its history, the City of Trondheim has been plaqued by large-scale fires. As a result, the wet or waterlogged levels are divided into layers hermetically sealed by silt and ash. The richly organic cultural levels are anerobic with a measured pH range of 4 to 6; neither bacteria nor fungal growth are supported.

Although dark and wet, newly excavated leather from the excavations is in good condition: it is relatively strong, flexible, easily handled, and with a low percentage of lamination. The variations in the degree of degradation during burial are a function of the nature of the leather material (skin type, quality, processing) and its history of use prior to burial as well as burial conditions.

The conditon of the affected leather varied. It was generally stiff, distorted, black, and often brittle resulting from previous conservation mediums which had since oxidised and dehydration during storage at -40°C for four years.

Previous Treatment

The affected leather items had been excavated and conserved between 1970-74. Early treatments consisted of working modified British Museum Leather Dressing in the form of a cream or an emulsion into the wet, insufficiently wet-cleaned leather. Later treatments consisted of dehydrating the wet-cleaned leather in acetone or ethanol for ½-1½ hr. followed by impregnation in 25% anhydrous lanolin w/v in white spirit or petroleum spirit 60° to 80°C for 1½-7 days. All treatments included a fungicidal agent: borax and boric acid in the early treatments and Preventol L (pentachlorophenol) or CMK (3-methyl-4-chlorophenol) in the later treatments.

SELECTION OF TREATMENT

Introduction

The problem of salvaging this large amount of previously-treated archaeological leather initiated a re-

search project to investigate, evaluate, and compare proposed methods of treatment. The quantity of finds requiring treatment imposed restrictions on the method of treatment selected as well as its execution. The objectives of the selected treatment were as follows:

- able to be carried out on a large scale such that batches of items could be processed at one time;
- impose minimal health and safety hazards to the operator and laboratory;
- preserve as much physical and chemical evidence as might still remain in the leather as possible;
- stability and reversibility; and
- economically feasible in manhours, equipment, and materials.

The problem was analysed in three stages: 1) removal of fungal growth; 2) extraction of previous conservation mediums; and 3) lubrication of the leather. Two comparative studies were undertaken: one examined the extraction of old conservation mediums; the other investigated lubricating mediums.

The leather contained an excess of nonbound fat which had been and would continue to be a factor in the degradation of the material following post-excavation treatment. Fortunately, all previous conservation mediums were based on the same compound - lanolin. Carlsson reported unsuccessful solvent extraction of British Museum Leather Dressing but did not name the solvents/procedures used [7]. Petroleum spirit 60° to 80°C, white spirit, and Genklene (stabilised 1,1,1-trichloroethane) are/have been used in lanolin-based lubricating mediums. These solvents were selected for the solvent extraction study.

The range of substances in use to lubricate leather is varied. There currently exist two schools of thought concerning the type of substance to be introduced: humectants versus substances based on fats/oils. The advantages and disadvantages of introducing these substances have been addressed by various studies. Both types have been used with archaeological leather. This study chose to investigate humectants, in particular, polyethyleneglycol (PEG) 400, glycerol, and sorbitol. Although thought not likely to bond to collagen other than by weak hydrogen bonds, these substances are chemically simpler and purer than fats/oils and theoretically reversible. Both PEG and glycerol are used widely in conserving wet archaeological leather in connection with solvent or freeze-drying. This study examined their application to dried-out, previously-wet archaeological leather. Various combinations of these two substances were also studied to determine whether a combination of properties could be obtained.

Materials

Extraction.   White spirit
                Petroleum spirit 60° to 80°C
                Genklene (stabilised 1,1,1-trichloro-
                ethane)

Impregnation.   Polyethyleneglycol (PEG) 400 - 15%, 20%,
                25% v/v in ethanol
                Glycerol (1,2,3-propanetriol) - 15%, 20%,
                25% v/v in ethanol
                Sorbitol - 15%, 25% v/v in ethanol at
                50°C
                PEG 400/glycerol - 10%/10%, 10%/15%,
                15%/10% v/v/v in ethanol

Samples

Leather samples used for testing were selected from the affected leather. Selection was based upon the year of excavation, i.e., previous treatment, and use, eg., shoe sole, shoe upper, etc., to achieve a representative sampling of the leather to be treated. The extraction study used cut-up unstratified leather to enable direct comparison; whereas, the impregnation study used unrelated intact pieces. Fifteen samples were processed for each treatment.

Conditioning

All samples were conditioned in accordance with ASTM D1610-69 (50±4% RH, 23±2°C) [8].

Procedure

Extraction. Some samples were mechanically cleaned with compressed air and brushing to remove the fungal growth; the remaining samples received no pretreatment. Samples were immersed in fresh solvent for 24 hr. This was repeated twice with the second bath subjected to periodic ultrasonic agitation. Treated samples were air-dried.

Impregnation. Samples mechanically cleaned and extracted with Genklene were immersed in the above-detailed solutions for seven days. The impregnated leather was dried in an ethanol-enriched atmosphere for 24 hr. followed by controlled air drying. Further study was carried out on the 10%/10% PEG/glycerol solution to determine an optimum duration of impregnation. Samples were immersed for 2,4,7,14 or 28 days.

Test Methods

To access the effects of the procedure the following properties were evaluated:

- Penetration - measured difference in weight
- Moisture content - dry oven at 99°C for 3 hr. after Hallebeek [9]
- Appearance - visual examination
- Flexibility - examination by simple physical manipulation
- Size - measured difference in dimensions
- pH - distilled water extract in accordance with ASTM D2810 [8] modified after Hallebeek [10].

Results and Discussion

Extraction. Similar results were achieved for each of the three solvents tested. None of the solvents were effective in removing the fungal growth. All solvents obtained a good range of colours of the leather material: Genklene results were on the light side whereas petroleum spirit results were on the dark side. Since organic solvents can result in the removal of tannins, the colour difference may, in part, be the result of such extraction; although, following burial for a prolonged period, remaining original tannins are less than 10% [11]. A range of flexibility was achieved for each solvent: Genklene-extracted samples were the most flexible and petroleum spirit-extracted samples were the least. The increase in flexibility was due to the removal of oxidised oils but it was acknowledged that one solvent type alone would not remove totally all the oils. The pH range was 5 to 6.

Genklene was selected as the extracting solvent based on these results, its properties as a hazardous chemical in comparison with white spirit and petroleum spirit, its compatibility with ethanol, and its regeneration through distillation [12].

Impregnation. The increases in sample weight as a result of impregnation are presented in Figure 1. The percent weight gain ranged from 12.6 for 15% PEG to 55.7 for 25% sorbitol. The changes were greater for glycerol and sorbitol and the percentages were at least twice that for the corresponding percent solution PEG. The samples impregnated with PEG/glycerol mixtures experienced a weight increase midrange between that experienced with only PEG or only glycerol. For PEG-impregnated samples there was a marked increase between the 20% and 25% solutions; this occurred for glycerol between the 15% and 20% solutions. The weight gain has remained constant for all impregnated samples.

The moisture content of the treated leather is reported in Figure 2 [13]. The range was 8.4% to 13.1%. The trend between PEG/glycerol-impregnated samples and those treated with PEG or glycerol alone reported for the penetration results was repeated. In contrast,

WEIGHT CHANGE (6 weeks)

Figure 1 showing weight change data with scale 20, 30, 40, 50 % increase:

Glycerol
- 15% — 27,2
- 20% — 43,5
- 25% — 54,9

PEG 400
- 15% — 12,6
- 20% — 13,4
- 25% — 21,4

Sorbitol
- 15% — 43,9
- 25% — 55,7

PEG/Glycerol
- 10%/10% — 26,3
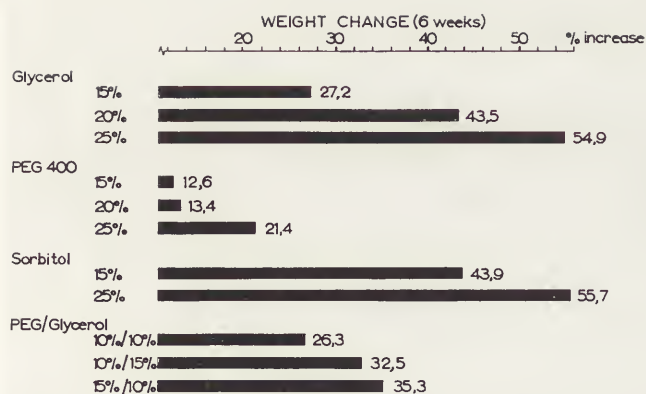- 10%/15% — 32,5
- 15%/10% — 35,3

Figure 1   Effect of impregnation on weight.

sorbitol-treated samples which had the highest weight gain had the lowest moisture content. All these figures are lower than the minimum 14% moisture content reported by Stambolov for vegetable tanned leather [14].

MOISTURE CONTENT (1 year)

Figure 2 showing moisture content data with scale 7, 8, 9, 10, 11, 12, 13, 14 %:

Glycerol
- 15% — 12,1
- 20% — 11,5
- 25% — 13,1

PEG 400
- 15% — 9,8
- 20% — 9,7
- 25% — 8,4

Sorbitol
- 15% — 8,4
- 25% — 8,9

PEG/Glycerol
- 10%/10% — 10,2
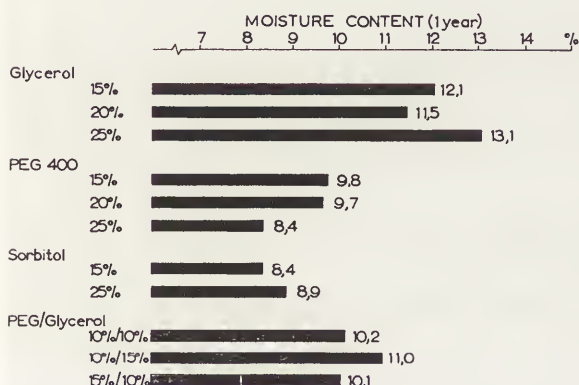- 10%/15% — 11,0
- 15%/10% — 10,1

Figure 2   Effect of impregnation on moisture content.

All impregnating mediums except 15% PEG produced an acceptable range of colours. Samples treated with 20% PEG and 15%/10% PEG/glycerol were lighter in colour than those of the other glycerol-containing solutions. Sorbitol-impregnated samples had a white surface residue resulting from the crystallisation of excess medium upon drying. None of the sample surfaces were damp but 25% glycerol-treated samples were cool to the touch. The surfaces of 15%, 20% PEG- and 15%, 25% sorbitol-impregnated samples were dry. A satisfactory range of flexibility was achieved for all mediums except the lower PEG percentages and sorbitol. Sorbitol results were stiff, hard, and brittle but also the fullest of all the mediums investigated. The lower percentage PEG results were stiff and compressed. Samples impregnated with glycerol and PEG/glycerol combinations except 15%/10% were full and rich in colour.

The effects of impregnation on sample dimensions are presented in Figure 3. All treatments produced an increase in dimensions of the samples from 1.8% for 15% PEG to 7.8% for 20% glycerol. As drawings of all the leather items as excavated (wet state) were available a comparison was made with drawings of the same leather before reconservation. The mean shrinkage was 11.3%. This gives a general mean shrinkage (excavated state versus reconserved state) of 3.5% to 9.5%.

The pH values measured were as follows: mechanically cleaned leather - 5.4; Genklene-extracted leather - 5.5; and 10%/10% PEG/glycerol-impregnated leather - 5.8. There was minimal change in the pH values throughout the treatment and the values lie within the recommended range of pH 4 to 6 [15].

DIMENSIONAL CHANGE (6 weeks)

Figure 3 showing dimensional change data with scale 0, 1, 2, 3, 4, 5, 6, 7, 8 % increase:

Glycerol
- 15% — 5,6
- 20% — 7,8
- 25% — 6,7

PEG 400
- 15% — 1,8
- 20% — 2,5
- 25% — 4,9

Sorbitol
- 15% — 5,3
- 25% — 5,2

PEG/Glycerol
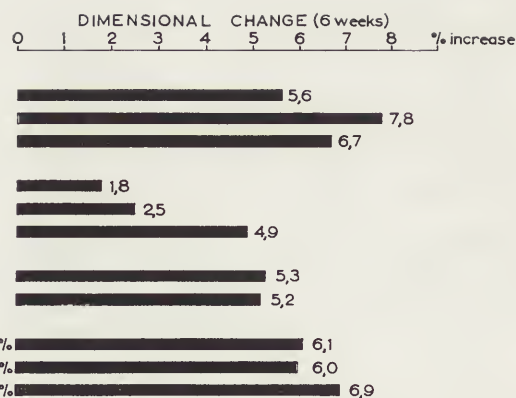- 10%/10% — 6,1
- 10%/15% — 6,0
- 15%/10% — 6,9

Figure 3 Effect of impregnation on dimensions.

The effects of varying the duration of impregnation in the 10%/10% PEG/glycerol solution were inconclusive. The percentage weight gain was not linear with time. Other factors such as thickness, condition, and object size must be considered. From the results it could be concluded that impregnation in excess of a few days did not achieve considerably more impregnation of the medium.

Although sorbitol was the most effective in bulking the leather samples, it was excluded from consideration for use based upon its need of an elevated temperature. Many of the PEG and glycerol solutions and combinations thereof produced acceptable results and satisfied the treatment objectives. Solutions of glycerol resulted in a more acceptable flexibility and appearance but the hygroscopicity of glycerol in higher concentrations is a negative factor. PEG 400 is not as hygroscopic as glycerol but requires higher concentrations to obtain similar colour and flexibility. The PEG/glycerol combinations did produce a combination of the qualities of these two substances. The 10%/10% PEG/glycerol solution was selected for the treatment.

IMPLEMENTATION OF TREATMENT

All affected leather items were mechanically cleaned with compressed air and brushing to remove the fungal growth. This operation was carried out in a standard air-abrasive chambre refitted to achieve maximum extraction and minimum risk to the operator. Items were placed by registration number into one or more expandable polyethlyene mesh bags and immersed into Genklene for 24 hr. This was repeated twice with the second bath periodically ultrasonically agitated. To the second bath was added 0.1% emulsifier (Secapur MA KONZ, Busing and Fasch) [16]. The first and second baths were reused. Each bath contained 20 litres of solvent which was regenerated through distillation.

Immediately after removal from the third bath the items were placed in a 10%/10% PEG 400/glycerol v/v/v in ethanol solution to which 0.25% Preventol O Extra (2-phenyl-phenol) was added. After three days the items were removed to an ethanol-enriched atmosphere for 24 hr. The treatment obtained acceptable and consistent results.

CONCLUSION

Large-scale urban excavations in Northern Europe continue to recover a vast quantity of wet archaeological leather. A direct consequence of this is the growing quantity of conserved archaeological leather in museum storage facilities. The preservation of this material is as dependent upon the method of conservation as its post-conservation history. This paper describes a case in which neither were adequate.

This study of a selection of treatment demonstrated that Genklene successfully extracted old conservation mediums based on lanolin and lubrication by impreg-

nation with a humectant, in particular, PEG 400, glycerol, or PEG 400/glycerol combinations in ethanol produced acceptable results. The conclusions are valid only for the methods and materials investigated which were selected based upon the case described. However, these conclusions may be applicable to other museums which have entrusted to their care quantities of conserved archaeological leather.

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SAFETY

A number of the chemicals reported in this work are hazardous and should be handled, stored, and used according to the manufacturer's product safety data sheets or an established hazard handbook.

ACKNOWLEDGEMENTS

LEATHER DRESSING: A MISGUIDED TRADITION?

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ABSTRACT

It is evident that the dressing of leather objects of all kinds is a popular and well-established tradition, yet there is a fair amount of experimental and practical evidence that it has little or no effect on leather's rate of deterioration (except for outdoors where water protection is necessary). It can be argued that the routine dressing of leather is hard to justify in terms of conservation principle because 1) it has little or no preventive effect when applied in the customary indiscriminate manner, and 2) there are so many potentially dangerous side effects. As a whole, leather conservation has not kept pace with the advances made in other conservation areas. Conservators working on leather objects must develop procedures which can be justified in conservation terms and treatments that are based both on relevant research and experience.

DRESSING TRADITION

Many conservators have begun to examine more closely the widespread use of leather dressings. For as long as one can remember, collectors, curators, and librarians as well as conservators, have applied dressings to their leather objects in what seems to be a time-honored tradition. It now appears, however, that most of these actions have been lacking in sound technical guidance. The quest to discover which dressing to use has seemingly distracted us from the more fundamental question: Should we be applying a dressing at all? What is the intended effect of the dressing application and what are its actual results?

The indiscriminate use of dressings on leather bound books and leather artifacts is indeed a long-standing practice. The ostensible purpose of such treatment has been:

1. To slow down deterioration;
2. To restore some of the leather's former strength and flexibility;
3. To improve the appearance of the leather.

The actual outcome, as this paper is intended to illustrate, is not usually the accomplishment of these goals. The person applying the dressing, however, rarely makes controlled observations on a short-term or long-term basis, and is therefore not aware of the actual results produced by treatment. Yet he or she feels satisfied that the dressing benefits and "preserves" the material.

UNDERDEVELOPED FIELD

At the core of the leather dressing controversy is the fact that by and large, the availability of sophisticated techniques for the treatment of this material has not kept pace with the advances made in other conservation areas. Within the fields of library and museum conservation relatively little attention has been given to the systematic preservation of objects made from leather. A new generation of technically-oriented conservators is helping to shed some light on this long-neglected problem by sharing the results of their work while searching for sound justification for each treatment.

Most advice on leather treatment, in general, has filtered down through popular articles and leaflets that do little more than recommend certain products or procedures, without providing a context to indicate whether those recommendations are supported by research results. Aside from these popular leaflets, there has been little dialogue between originators and users of the information. Individuals charged with preserving this complex, organic material no longer can accept anonymous recipes, but must instead require treatment policies which are based on sound scientific understanding.

IMITATION OF INDUSTRY

Much of the existing practice regarding leather dressings stems from a direct imitation of leather manufacturing procedures. This oversimplification does not generate appropriate conservation treatment, primarily because of the dissimilarity between the characteristics of historic leather and those of hides during tanning. The objectives of the leather conservator also differ vastly from those of the commercial tanner who is involved in lubrication as a step in the tanning process (e.g., fat liquoring, and stuffing of wet hides). Furthermore, bonding of the lubricant to the collagen fibers is crucial. Conservators most often are not able to monitor this process nor assure the effectiveness of the treatment.

The American leather chemist, George H. von Fuchs, who has helped to develop the industrial lubrication process, has written, "The primary function of a leather lubricant is to prevent the adhesion between the leather fibers that takes place when wet leather is dried." (von Fuchs 1957, p.550) His work showed that effective lubrication can be attained by coating the fibers with surprisingly small amounts of lubricants.

He goes on to say, "By the time leather is dry, most of the oil absorbed by the leather has already served its purpose, since it is not needed for lubrication. As a matter of fact, the leather would be better off without it. However, a small amount of lubricant is needed (a) to prevent cross linking of leather fibers on rewetting with water with consequent hardening of the redried leather and (b) to strengthen the leather." von Fuchs then stipulates, "...the minimum for lubrication is in the neighborhood of a few tenths of one percent on the dry-leather basis...the larger amount (of 5%) was not for lubrication but for imparting water resistance." (von Fuchs 1957, p.559)

An important consideration is that a leather artifact in a museum collection is no longer required to function as was originally intended. In most instances, flexibility is not a primary, desired characteristic when the object is no longer required to flex. Often, original flexibility need not be restored and lubrication can be considered unnecessary. Furthermore, an increase in fat content will only affect flexibility if the leather's inflexibility is not caused by irreversible changes in the material such as the breakdown of the polymer structure or oxidation of lipids. The excess of lubricant that has been added traditionally to leather for waterproofing (and indirectly to prevent resultant mold and weakening) is usually not needed in museums of libraries where conditions are dry.

Despite the objection to the current indiscriminate practice of leather dressing, we agree with most leather specialists that a certain amount of lubricant is useful in preserving leather. In practice, only very small amounts of lubricants need be introduced into historic leather. Most importantly, the oils and fats must achieve thorough penetration of the leather and become evenly distributed. As P. Hallebeek and H. Von Soest have clearly pointed out, "But even if the right amount of oil is used but the oil is nonetheless not evenly distributed in the leather texture, the effect of the oiling cannot be rightly considered to be a preserving one." (Hallebeek 1981)

With all books, and in many cases involving museum artifacts, only the grain side of the leather is accessible for lubrication. Since the grain side is much less permeable than the flesh side, it would be unrealistic to expect an even distribution of the lubricant in all cases.

RESEARCH ON LEATHER DRESSING

The effect of leather dressings on permanence has occasionally been studied directly, and sometimes worked on as part of a larger experiment. Almost inevitably the researchers have concluded that the dressing had no preservative effect. (Smith 1964) One study found that chestnut-tanned leather treated with sulphonated cod liver oil deteriorated faster than untreated leather. (Wallace 1935) The British Leather Manufacturers Research Association (BLMRA) came to a similar conclusion after their own study in 1945 (Innes 1945, pp.446-7):

> There seems to be a general impression
> that grease exerts a preserving effect
> on vegetable-tanned leather.
>
> In examining three pairs of bookbinding
> leathers, stored for 40 years in the
> British Museum Newspaper Library, one
> member of each pair being rotted and
> the other sound, it was observed that
> the proportion of grease in the leathers
> did not run parallel with durability.

This study shows:

> ...not only that in two pairs the
> rotted leathers contained far more
> grease than the sound, but also that in
> all three cases the good leathers had
> remained sound in spite of containing
> only 1 percent of grease or less.
>
> The bulk of the evidence thus shows
> that grease up to the amounts usually
> found in practice has no preserving
> effect, though it may help to lubricate
> the fibres of a leather deficient in
> grease.

In a more recent BLMRA work, R.G.H. Elliot included degreased leather in a long-term natural-aging study, and found that the absence of grease did not make it more prone to decay. (Elliot 1969)

Another study by Hannigan, Naghski and Windus found a slight beneficial effect from certain dressings. (Hannigan 1965) This study compared the results of four different dressings applied at two-year intervals for 34 years on both chrome-tanned and vegetable-tanned leather bindings--a thorough and fair test, likely to show up an effect if there were one at all. Measures of deterioration used were tensile strength, slit tear, soluble nitrogen, soluble sulfate and pH, of which the slit tear test was judged to be the best measure of deterioration.

The four dressings used in this study were:
1) vaseline, 2)neatsfoot oil and lanolin in 60:40 ratio, 3)oil and tallow emulsion in water, and 4) a mixture of lanolin, wax, castor oil, sodium stearate and water. The authors concluded that although the dressings provided some protection to all the leathers, "Their use was not adequate to prolong the life of the vegetable-tanned leather effectively." (Hannigan 1965) They mentioned this because most leathers for bookbinding are vegetable-tanned.

POTENTIAL PROBLEMS CAUSED BY DRESSINGS

Conservators often note that the historic leathers they treat are over-oiled. Excessive oiling is to be expected when indiscriminate and repeated dressing has been practiced for years. Unfortunately, as a result of these good intentions, the problem is compounded, and the "preservative treatment" itself leads to further deterioration of the object. Not only does over-oiling impede future conservation

treatments such as resin impregnation and adhesion mending, but it has been shown to weaken the leather. Hallebeek and von Soest point out that the result is that water is driven out and the leather's moisture content is lowered, risking desiccation. (Hallebeek 1981)

In practice, the dressing of leather is largely an irreversible procedure because of the deep penetration of the foreign ingredients and the solvent's transport of existing soluble components through the leather.

Instability of the specific fats, oils, or dressing additives, as well as the type of solvent or vehicle selected can also be directly responsible for numerous undesirable and unforeseen side effects.

Oils and fats can: encourage biological deterioration
form unstable spews
become very acidic
oxidize and stiffen
discolor and stain
leave a sticky surface
wick into adjoining material
Wax additives can: encourage biological deterioration
block surface porosity
discolor and collect dust
impede further treatment
change the surface appearance
Dressing solvents can: affect surface finishes
wet, swell, and deform leather
dissolve or dislocate original
tanning components

UNDERSTANDING THE NEEDS OF EACH LEATHER OBJECT

The complexity of leather as a material must be understood. Its preservation depends upon having a clear understanding of a number of factors. The decision to augment a leather's fat content by lubricating should depend on determinations and calculations specific to the particular leather including: 1) its animal origin, 2) its mode of manufacture, 3) its chemical and physical condition, and 4) its future use and conditions of storage.

Only a few laboratories have realized the need for careful determination of the existing and required fat content in order to establish whether dressing is required. The dressing should not be applied haphazardly; rather the proportion of fat added to a dressing solution should be calculated on the basis of the extracted and weighed fat content of the specimen. The amount and type of both solvent and lubricant added should also be consistent with the physical effects desired.

It is clear to those working within the field that more non-destructive analytical procedures for measuring fat and oil content must be developed. The time has come for conservators working on leather objects to develop sound procedures which unequivocally accomplish our goals. Those of us charged with the treatment of these historic materials in our libraries and museums must be confident that every action is justified in conservation terms and is based on both relevant research and experience.

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RESTORATION OF CHINESE AND INDONESIAN SHADOW
PUPPETS

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SUMMARY

Warn off parchment parts of which the puppets
are replaced by patches of new parchment, but
of the same thickness as the original. Parch-
ment used for the restoration of Chinese pup-
pets, is dyed on either side with dyestuff
because these puppets are and should remain
transparent. The binding medium for these
dyes is an alcoholic liquid of egg white, ox
gall and sugar. Damaged Indonesian puppets,
which are, as a rule, coated with tempera
paint and therefore impervious, are restored
by fixing the cracked paint layer with dilu-
ted egg white followed by burnishing with a
hot spatula. On the other hand crumbling
paint is sprayed with diluted starch size and
pressed flat.

The earliest description of shadow puppets as
protagonists in a play dated from 145-86 B.C.
and it shows the sorrow of the Emperor Wu-Sah
after the death of his wife.

The shadow puppets theatre, involves the pro-
jection of shadows on a screen of cloth on
the back side of which the audience by wat-
ching the shadows, follows the play at issue.
The puppets employed in the shadow theatre
are cut out of the skins and hides of young
animals, preferably from those of sheep,
calf, mule and buffalo, which prior to de-
signing the puppets on them, must be pre-
pared in a manner similar to that of parch-
ment making. Suitable parchment for the ex-
cision of puppets should not surpass the fol-
lowing limits: in the case of Chinese puppets
the thickness of it lies usually between 0,1
and 2 mm. awhile for the Indonesian puppets
the parchment should be from 0,5 to 1,5 mm.
thick.

It is a distinctive element in this craft
that the design on the Indonesian puppets
(fig. 1 and 2.) -sometimes in relief- is
drawn on the parchment with tempera paint,
i.e. mineral pigments and egg white.

On the other hand the Chinese puppets must be
transparent, as demanded by the ethnic tradi-
tions on which their shadow-theatre rests.
Therefore they are decorated with dyes. Still
another peculiarity is that there are two
types of Chinese shadow pupptes:
The Peking puppets (fig. 3.) and the Setchuan
puppets (fig. 4.). The difference between
them seems to be a subtle one and for the
present text only the difference in thickness
of the parchment is of any importance.

In the art of puppet making the outline of a
puppet is drawn with a steel needle on the
parchment. After that the parchment is laid
on a layer of wax and the outlined figure is
cut out with a knife. The figure is washed
with water and left to dry in a shaded space.

Next, the not entirely dry parchment is rubbed
with a wet cloth for additional wetting, the
pattern of a design is placed on it, and incis-
sion is carried out. The puppet is then
flattened out by placing it under a wooden
board, and cleaned from any dust, that might
have meanwhile settled on it, as otherwise such
dust would interfere with the subsequent pro-
ces of dyeing.

Traditionally natural dyestuff extracted from
various plants and dissolved in water of alco-
hol or both, with the addition or animal glue,
is used for dyeing. The puppets are dyed on
either side, dried, and then flattened by means
of a pressing iron. A permanent flattening of
the puppets is attained by putting them for a
while in a press. The parts and ornaments be-
longing to a particular puppet are at that
stage assembled and tied together with catgut
strings.

A particular aspect of the Peking type of pup-
pet is that the parchment of it is additional-
ly treated with the juice derived from the
Chinese woodoiltree. This oil hardens even
faster than linseed oil and in doing so in-
creases the transparency of the parchment.

The shadows-theatre unsually dramatizes folk
epics so that the conflicts in which the pup-
pets are involved during performances, even-
tually causes a noticable physical damage to
them.

The major restoration concern with this theatre
requisite is the completion of mutilated or
warn off puppets. Lacerated parts should be re-
placed with parchment of the same thickness as
the one of the puppet proper. To that end the
matching pattern is excised from the some what
dampened parchment with a scalpel. It is impor-
tant that the parchment for supplementing
should bear no defects and to avoid such mishap
one is well advised to outline the defective
area beforehand, by scrutinizing the parchment
which is best done when the parchment is placed
on a prooflight viewer. In order to achieve an
equal dyeing on both sides, the flesh side of
the excised patch must be burnished and this
is done through dampening and pressing the
parchment. Margins at which supplements and
old parchment are supposed to meet must then
be rendered thin by shaving, and the whole
patch is brought to the proper color with the
so-called "clear egg white dyestuff". For the
preparation of it an egg white is beaten into
foam, and the clear fluid that oozes out of
the foam is diluted with water in the ratio
1 : 1. Beside the diluted egg white, a solution
of ox gall is also prepared by allowing 50 g.
of ox gall to be swollen and gradually dis-
solved in 950 g. of pure alcohol for about 15
minutes. The ox gall solution is filtered and
then included in the formulation of the dye-
stuffcarrier, as noted below:
10   ml of diluted egg white
 0,5 ml of 5% solution of oxgall in alcohol
 1   knife point of sugar (plasticizer and
     cohesion promotor)

The three ingredients are mixed with the de-
sired dyestuff (in this context Coranil-Farb-
stoffe, Hoechst AG, Frankfurft a. Main, West
Germany) and applied on either side of the
patch. The parchment must be dampened before
dyeing for the attainment of a deep dyeing and
dyed, and after that allowed to dry. The
dyeing is carried out with a very low percen-
tage of dyestuff liquor and it is through re-
petition that the color of the original parch-
ment could be matched. The supplements dyed
thus, are glued to the puppet with the above
egg white - ox gall - sugar adhesive, awhile
the mobile supplements are tied to the origi-
nal with catgut snare.

Although at first sight similar to the Chinese
the Indonesian puppets (painted and therefore
not transparent) require a quite different re-
storation care. Cracked paint layers on the
puppets (fig. 5.) are kept from flaking off by
consolidation with diluted egg white (one egg
white is dissolved in 60-70 ml. of water and
left to stand for 24 hours in a covered vessel).
This fluid is painted on the damaged areas
with a soft brush and the wet areas are then
covered with silicone relined paper and pres-
sure-fixed with a hot spatula (the temperature
of which should correspond to the mark: syn-
thetic fabrics on the dial of a pressing iron)
(fig. 6.)

If, however, the cracking of the paint is so
advanced as to flake off, at the touch of the
brush (fig. 7.)it is treated differently. In that
case it is sprayed with diluted starch paste.
For this kind of consolidation a commercial
brand of starch, that is: Eukalin BKL (Firma
Gebr. Wachler, 5100 Aachen, West Germany) is
used, but a home-made starch paste is stirred
in a mortar with 80 ml. water for as long as
it turns into a smooth fluid. The adhesive is
then filtered through a nylon stocking and is
ready for use. The damaged areas of the puppet
are disengaged from one another by removing
the horn buttons which hold the puppet parts
together. This is easily done if in advance
the edge of the parchment around the buttons
has been moistened with a softening agent such
as the "Lederweicher SR" (Fritz Minke, Post-
fach 527, 4100 Duisburg-1, W.Germany). The
puppet parts are then laid on a board which
has already been covered with a thick layer of
newspapers, followed by a white blotting paper
and topped with silicone relined paper. The
puppet parts are sprayed with the adhesive
fluid, turned over and sprayed again on the
other side. Another board with the same news-
paper - blotting paper - silicone paper lining
is put on top of the puppet part, and the whole
sandwich is inserted in a press, and pressed
in it for at least 24 hours (fig.8.). Any
remnants from previous oiling on the puppet
should of course be removed before spraying as
otherwise the starch size would nog adhere to
the object.

Broken filigree on the puppets is restored by
gluing together the disjoint parts with cyano-
acrylic adhesive (Kö-Kleber C2, Firma Kömmer-
ling, Chemische Fabrik KG, 6102 Pfungstadt,
W.Germany). Whereby thorough cleaning of the
part with aceton before adhesion is obligatory.

Missing elements like buttons, filigree net-
work or other parts of a puppet should be re-
placed with replicas, made, preferably, of the
same material. As far as the pratice described
above is concerned, however in some instances,
missing horn buttons have been reproduced in
wood, and to judge from subsequent observations,
to the same effect.

Photos courtesy Christel Knetsch, Deutsches
Ledermuseum, Offenbach am Main, W.Germany.

fig.1. A puppet from Java, Indonesia
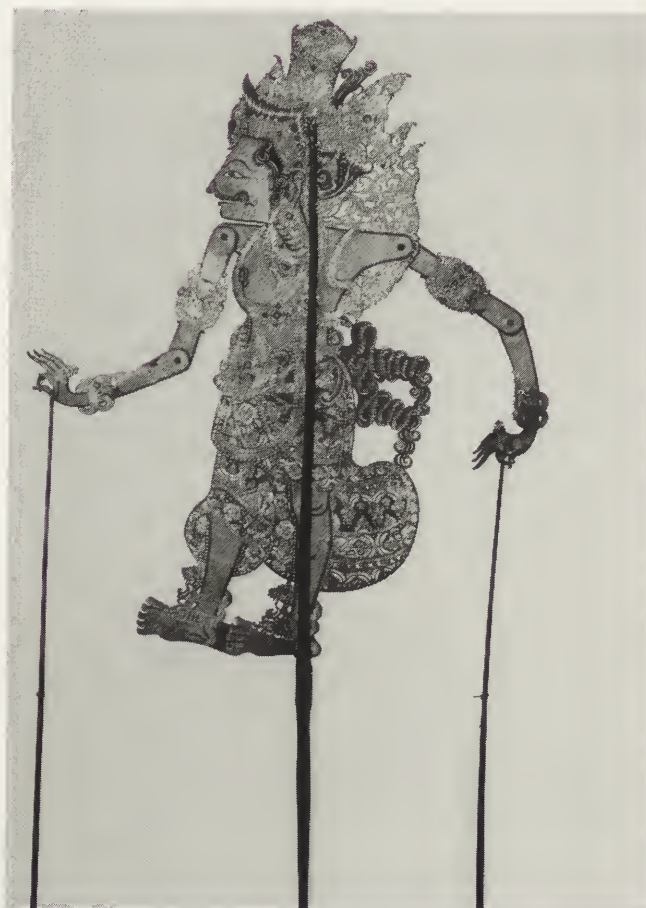
fig.2.　A puppet from Bali, Indonesia

fig.3. A puppet from Peking, China

fig. 4. A puppet from Setchuan, China

fig. 5. Chracked paint on an Indonesian puppet
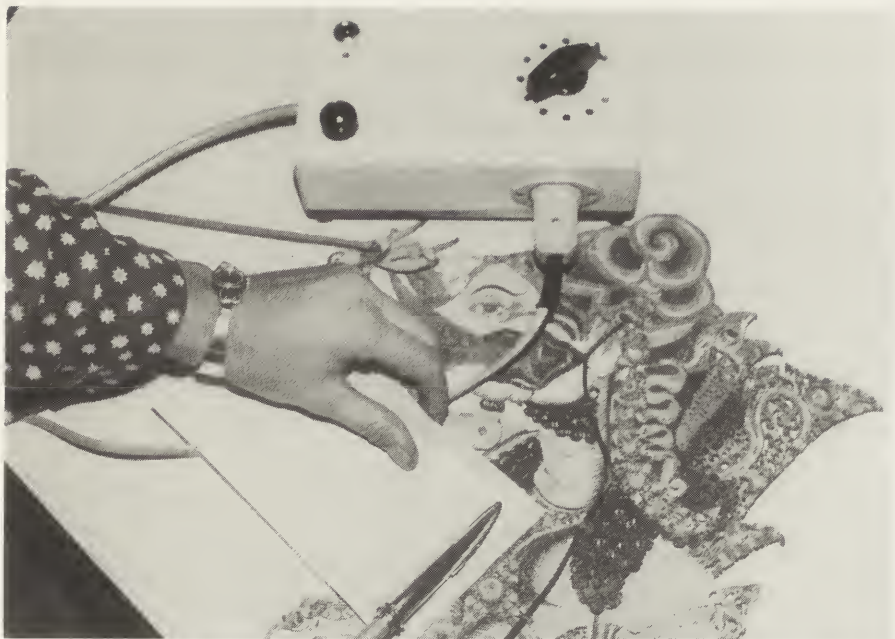
fig. 6.
Restoration of cracked
paint with egg white and
pressure-fixing by means
of a hot spatula.

fig. 7.
Advanced deterioration of
paint layers.

fig. 8.
Consolidation of crumbling
paint by means of starch-
containing spray.

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Current Research into the Conservation of Frozen Skins from the Arctic

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Summary

Recent archaeological work in the Canadian Arctic resulted in the excavation of skin artifacts and created the need for a conservation process to treat skins that are frozen, distorted and contaminated with natural fats and minerals.

A research group consisting of conservators and scientists was formed at the Canadian Conservation Institute (CCI) to develop appropriate methods of studying the skins and of cleaning and stabilizing them. This paper gives an overview of how the problem is being approached, what is presently being done, and what we hope to achieve.

The intention is not primarily to report results, but rather to report the approach, procedures, some preliminary results, to make others aware of what is being done; and to solicit comment and input.

Introduction

Archaeological excavations in the Canadian Arctic over the past several years have produced a number of skin artifacts which are important for the interpretation of the early Eskimo culture. The artifacts are, in most cases, articles of clothing such as boots, mittens or parka fragments which are made from sealskin, caribou or polar bear hide. Because they have been buried in permafrost, their condition tends to be good, especially when the soil environment is heavily contaminated with oil and fat deposits[1]. The archaeologist can only excavate when the ground has been thawed, this means that the artifact when excavated is wet, dirty, and often very fragile. They may also be contaminated with bacteria which could lead to putrefaction and might be hazardous to people. To minimize this risk and to prevent the objects from drying out and distorting, the skins are frozen or chilled immediately after excavation. Skins excavated to-date have been so treated, however, this means that they still require cleaning, conservation and reshaping before they can be used for study or display.

By 1982, the Archaeological Survey of Canada had a number of such artifacts in storage and further excavations in the Arctic were planned and expected to produce more material; as a result it became necessary to develop methods of cleaning and conserving this material. Although well documented treatments exist for tanned archaeological leather[2,3,4], there is little or no information on the conservation of untanned archaeological skins.

Faced with this problem and ever cognizant of the desirability of having scientist and conservator work closely together, in 1982, the CCI assigned a team of biologists, chemists and conservators to study the condition of skins excavated from Arctic sites, and to find ways of cleaning and preserving them. It was believed that the results and tech-niques from this study would also have application in the conservation of waterlogged skin and leather from wet sites and flooding disasters.

Development of a Research Programme

A. Characterization of Archaeological Skins:

The meaningful evaluation of a new conservation process, requires methods to describe fully the nature and condition of a material at all stages of a treatment. In the case of the skins, it was decided to utilize our existing expertise in biology and develop a microscopical characterization scheme, which we believed would provide the most information on the identification and evaluation of the skins. This evaluation provides a means of characterising some of the changes that have and can occur in the physical and chemical integrity of an artifact, and hence describes it more precisely. Moreover, using the same techniques it is possible to monitor the progress of conservation treatments and identify interaction between the materials used in the process and the skins.

Microscopical and microchemical examinations of skins based on established histochemical techniques[5] are being used to identify and comment on the condition of such skin components as ground substances, lipid material, inorganic inclusions and elastic tissue. Epidermal slippage and collagen fibre bundle breakdown can also be assessed. This latter phenomena is also being investigated by studying the swelling and thermal characteristics of collagen. For example, collagen shrinkage temperature measurements are being investigated as a means of showing how particular detergents or surfactants used in washing treatments can effect the structural cohesion of the collagen fibres.

This microscopical and microchemical characterization scheme is being developed and refined as the work continues. However, it is believed that the ability to show the presence or absence of many of these features and to understand better the chemical, physical and morphological properties of skin artifacts will prove to be of great value in this and other similar projects.

B. Cleaning of the Skins:

The skin samples used for the study are from Thule Eskimo occupation sites on Somerset and Devon Islands; their estimated date is 1100 to 1500 A.D. As a safeguard against possible health hazards, the skins were sterilized using gamma irradiation before research began.

Microscopical examination, looking at such features as the hair scale pattern on the hair follicles, follicle patterns and grain patterns, identified the skins as sealskin and showed that, with some skins, the fibre structure was well preserved and the skin still retained fur. All the skins, however, were covered with miscellaneous burial debris and encrustations containing fat and mineral deposits. These could be white and compact, brown and greasy or have the consistency of butter. Infrared spectrophotometry showed the deposits to be a mixture of the calcium salts of fatty acids and calcium carbonate, silicates were also present. This material was also embedded within the matrix of the collagen fibres.

Although the fatty material does appear to give the skins a flexibility uncommon to most archaeological skins, little is known of its long-term stability. The fatty material could, for example, be more prone to biological deterioration. It also gives the artifacts an unattractive appearance and smell. Also, if the crystalline material embedded within the collagen matrix is not removed, serious problems could occur due to abrasion when the skins are subjected to handling.

The microscopical evidence convinced us that the removal of the dirt, fat and mineral deposits from both the surface and internal structure of the skins was of major importance for the long-term stability of the skins. Thus a search was begun to find a cleaning method which was safe, and simple to use; and which did not alter the chemical and physical integrity of the skins. The leather technology[6] and the leather[2,3,4] and textile[7,8] conservation literature were reviewed for cleaning agents which were chemically neutral. The following - water, ethanol, Varsol®, Shellsol®, Synperonic N®, sodium dodecyl sulphate (SDS) and the disodium salt of ethylene diamine tetra-acetic acid (EDTA) - were tested separately, in combination, or together with mechanical cleaning.

Preliminary screening experiments showed that, of the systems evaluated, a wash solution combining a detergent (SDS or Synperonic N®) together with EDTA, gave the best cleaning action. The EDTA releases the calcium associated with the fatty acids, collagen fibres and calcium carbonate; the detergent softens the fatty deposits, which facilitates the penetration of the EDTA into the skin and allows for easier removal by mechanical methods.

To monitor the treatments, samples of the skin and wash solutions were taken at regular intervals for pH, protein and microscopic analysis.

Having shown that this washing solution combination was promising, it was necessary to optimize the system in terms of detergent type, pH, temperature, duration and number of washes. As this paper is being written a series of experiments are being completed to study these parameters. They are being carried out on several seal skins representing a wide variation of skin thickness and degree of degradation. The experimental treatments are again being compared on the basis of microscopical, pH and protein analysis of samples taken before, during and after treatment.

C. Drying:

Uncontrolled drying of the skins leads to shrinkage and distortion. Before the importance of cleaning procedures had become apparent the effects of freezing and methods of freeze-drying had been a principal focus of the research project, since freeze-drying had been previously used for skin and leather[3,4] and freezing remains the preferred method of storing the skins between excavation and treatment.

To evaluate the freeze-drying treatment standard size samples are taken from the cleaned skins and freeze-dried. Dimensional stability is assessed by measuring shrinkage compared with air dried samples; weight loss is measured and cross sections before and after drying are examined by microscopy to determine any changes that occur during freezing and freeze-drying.

Conclusion:

This paper has attempted to describe the development of a research programme and the methodology adopted to find a conservation process for frozen archaeological skin artifacts excavated from the Canadian Arctic.

As the research continues we hope to answer the following questions which have arisen from this study and which might have impact in preserving skins and leather in similar conditions but from different contexts.

1. How do the fatty acids and calcium carbonate affect the stability of the excavated skins? What amount must be removed before the skins can be considered stable and what is the best compromise between artifact stability and the cleaning necessary for archaeological examination and display?

2. What is the most suitable detergent system for cleaning fragile archaeological skins?

3. Can shrinkage temperature tests be used to determine the effects of detergents on the skins?

4. Will it be necessary to replace the extracted fats with a lubricant such as polyethylene glycol? Will the addition of PEG create unstable conditions in the skin?

5. What are the effects of freezing and freeze-drying on the structure of the skins? Will it be necessary to add polyethylene glycol to reduce drying stresses or shrinkage?

The work is still in its infancy and only preliminary results have been given. We hope, however, that this paper and the presentation that will follow, will provoke comment and suggestions from others working in this field.

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CHEMICAL SOLUTIONS OF PROBLEMS ENCOUNTERED IN THE CONSERVATION OF OLD LEATHER.

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SUMMARY

The traditional practice to procure old
leather with buffers for the purpose of pro-
tecting it against further attack issuing from
acidic sources is critically examined and
wherever necessary revised. History-cases
are discussed and used as a means to illus-
trate the author's point, that buffering is,
at best, a conservation measure of relative-
ly short duration.

If excessive acidity in leather objects kept
in polluted environment is to be expected, it
is well advisable to measure both the pH of
the leather and its content of ammonium sul-
phate. Ammonium sulphate, being the end pro-
duct of the degradation, caused by the re-
action between the proteins in the leather and
sulphuric acid (from the air pollution or from
other sources) may be accumulated in large
amounts in old leather. As such it would serve
as a reservoir for sulphate ions. These ions
determine in fact the acidity of the leather,
and later -after conservation- they would even
interfere with the buffer system brought into
the leather with the purpose of guarding the
pH.

That information about the content of ammonium
sulphate is important, may be concluded from
our analysis of samples taken from the gilded
leather in the castle at Rhoon, near Rotterdam;
an area heavily industrialized and with in-
tense infra-structure. The gilded leather
wall-hangings in that castle contained 12% by
weight of ammonium sulphate.

Detection of ammonium sulphate: In a sample
from the extract intended for the measurement
of the pH several drops of 1% barium chloride
are added, in order to test whether ammonium
sulphate is present. If this is the case,
then the quantitative measurement of ammonium
sulphate is carried out as follows: The pH of
the water extract from a weighed leather
sample is adjusted to 5,5 with a 0,1 N solu-
tion of sodium hydroxide. To this extract are
added 25 ml of a 20% solution of methanal
(formaldehyde) in water, which prior to use
must be neutralized with 0,1 N sodium hydro-
xide. A pH-meter or thymolblue-indicator will
establish the pH-value. Both extract and
methanal are then titrated with 0,1 N sodium
hydroxide in the presence of a pH-indicator
up to 7,0. In the described test the methanal
reacts with ammonium ions and forms a weak
acid, which depresses the pH-value of the so-
lution. This pH-depression reciprocates to the
amount of the acid formed thus, and the latter,
in its turn, reciprocates to the amount of
ammonium ions. Calculation:

$$\% \ (NH_4)_2SO_4 = \frac{X \ ml.NaOH \times 0,66075}{\text{weight of leather sample}}$$

Unduly acidic leather must, of course, be
brought in the safe pH range of 3 to 6. In our
practice we as a rule achieve this adjustment
by fumigating the leather in question with
ammonia for about 15 minutes. As prolonged
exposure to ammonia is hazardous for the health
care should be taken that the ammonia in the
fumigation container (cupboard, plastic bag,
chamber) can be easily evacuated after use.

The penetration of ammonia in circumstances
concerning us here, is quite satisfactory. It
penetrates in the leather even through layers
of paper pasted on the back of it, as a rein-
forcement. The evidence of this we could
notice last year during the treatment of the
gilded leather wall-hangings in the castle at
Dunster, England, when removal of its paper-
lining was considered to be so risky, that we
had to fumigate the whole sandwich (gilded
coating - leather - paper lining). And with
remarkable success as the subsequent tests
showed.

Another example of the good penetration of
ammonia is the fumigation of a leather frame
of a painting belonging to the museum "Maurits-
huis" in The Hague. For the sake of stability
the leather frame was nailed to a rigid wooden
frame, in such a way that the interface
leather / wood seemed to us quite inaccessible.
However, after fumigation we did detect there
ammonia in amounts that were high enough to
correct the excessive acidity of the leather
frame.

From our experience so far we may report,
that directly after fumigation with ammonia
the pH of the leather is approximately 8 or 9.
Several hours later, however, it is found to
have sunk to pH 4 or 5, and remains so per-
manently; that is, if no fresh acidic material
would enter it.

But as this is rarely the case, counter mea-
sures must be taken in order to avoid any pos-
sible acidic influence on the pH of the leather.
And this is best done by the employment of
buffers. If buffers are omitted, however, the
pH of a fumigated leather will continue to
sink and eventually will become too acidic for
the upkeep of the leather. A confirmation of
such danger we observed in the pH-values we
measured on samples of the gilded leather in
the aforementioned castle at Rhoon. Regular
testing in the course of 2 years showed that
at first the pH sank rapidly from 4,5 to 3
and then slowed down, but still went on
sinking. At the end of the second year the pH
of the leather was 2,1-

So the use of buffers is an important conser-
vation factor, and the only question is which
buffer should be used?

The popular buffers like the alkali lactate,
citrate or tartrate perform very poorly, and
are, therefore unfit for the objective we pur-
sue. What we mean by that is that considering
the large amounts of ammonium sulphate in old
leather exposed to air pollution, the above
mentioned compounds, commonly used in dressing
procedures are quite insufficient to counter-
act the acidity ensuing from both the environ-
ment and the dissociation of ammonium sulphate.
Yet it is obligatory that the presence of am-
monium sulphate should be taken into account.
It represents the effect of sulphuric acid on
leather and the 12,0% of the salt found in
gilded leather in the castle at Rhoon is cal-
culated to correspond whith 80 g of concentra-
ted sulphuric acid per square meter of leather.
To buffer this amount of sulphuric acid the
following quantities of chemicals, again per
square meter are needed:

potassium citrate	205 g
sodium lactate	204 g
sodium-potassium tartrate	328 g
imidazole	109 g

Provided that the concentration of the buffer solution amounts to the usual 2%, we generally employ, then for the purpose of counteracting the sulphuric acid, there would be needed at least 10 lt. of potassium citrate in each square meter of leather. And in the case of imidazole - not less than 5 lt. No leather would,however, absorb such large quantities of liquid. On the other hand, increased buffer concentration, would mean high viscosity of the solution, which as a consequence would only superficially penetrate into the leather.

An alternative in view of this difficulties, may be to decide to use only 1/3 of the above estimated buffer solution and to accept that its buffering effect would last only 1/3 of the time that the ammonium sulphate had taken to accumulate.

Reasoning thus we came to realize the relative benefit of these buffers and the need for repetitious buffering. And as far as reliable conservation is concerned we prefer imidazole as a buffer for leather.

Imidazole, HNCHNCHCH, a dinitrogen ring compound of pK (extent of dissociation) 6,95, is soluble in water, alcohol, aceton, ether etc. and reacts also as a weak acid which is the requirement, a buffer must satisfy. It is used as such in biochemical processes. Besides, imidazole is hygroscopic and once in the leather it therefore also functions as a humectant. With metals as iron and copper, imidazole forms insoluble salts, the consequence of which may be that, traces of these metals, in the leather blocked thus, by imidazole, would not catalize the oxidation of sulphur dioxide, obstructing in this way the formation of sulphuric acid. Imidazole, moreover belongs to the group of chemicals called antihistamines, which enables it to "antagonize" insects and accordingly to protect its surrounding from their attack.

Because imidazole is soluble in both water and organic solvents, it can be quite easily added to oil emulsion as well as to dressings in organic solvents; in the latter case imidazole is first dissolved in isopropyl alcohol, and this is then mixed with white spirit Shell soll K (a Shell solvent of very low aromatic hydrocarbon contents).

How we would apply imidazole is always determined by the condition of the leather that needs treatment.

For instance, we treated the gilded leather wall hangings in the Royal palace "Het Loo" at Apeldoorn in two stages. First we impregnated it with an oil emulsion without buffer (the reason for this being that imidazole in the emulsion, fixes the pH of its water phase at 8,5 which tends to darken the leather). Then followed the application of imidazole, as a 2% solution in isopropyl alcohol combined with white spirit.

The leather frame already discussed above, we conserved in the traditional way, which is: through impregnation with a dressing of the composition:
2% imidazole
6% oil (neats-foot oil: lanolin in the ratio
    4 : 2)
All dissolved in white spirit of very low aromatic hydrocarbons content).

However, in the case of the gilded leather wall-hangings in the castle of Dunster, which in fact were treated with a dressing similar to the one just specified above, we thought it necessary to increase the contents of imidazole and oil respectively to 4% and 12%. This measure was motivated by the presence of paper lining which absorbs and keeps some quantities of both materials. The reason for the adaption of the formulation of the dressing lies in the fact that the loss of imidazole and oil, should not happen at the expense of the gilded leather.

Finally we wish to point out that products like neats-foot oil, not always are delivered pure. In some instances in the past we had reasons to suspect that the neats-foot oil was deliberately mixed with other, not specified, oils, which, for all we knew might have been drying oils. In view of the harmful consequences, which may follow from the use of such oil blends, we suggest that the oil one intends to employ in leather-conservation be checked beforehand. For the quality control of the neats-foot oil we use the following essential data:

Fac. (color)	: < 1
Gardner (color)	: 3 à 5
Free Fatty Acids	: 1,02%
Iodine Value	: 71,5 (should be: 67-81)
Saponification value	: 198 (should be: 190-200)
Not Saponifiable	: 1,00% (should be: 0,3%)
Cloud Point	: -7°C

When the jodine value is to high > 81, you are dealing with a mixture from neats-foot oil with possibly rape seed oil or soya oil or other vegatable oils.

Leather frame ca. 1630 of a painting:
Embossed, Museum Mauritshuis, The Hague.

THE FREEZE-DRYING OF LEATHER PRETREATED WITH GLYCEROL

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Summary

In recent years a large quantity of leather has been
excavated at a number of sites in London. In 1983
alone over 1000 objects were treated by the Conservation
Department of the Museum of London. This has provided
ample opportunity to develop methods for the treatment
of leather in bulk without compromising standards.
This paper describes the procedures now employed. In
addition the opportunity has been taken to review some
aspects of freeze-drying treatments carried out 3-4
years ago and previously published (1) and to report
on further investigations into the effects of glycerol
as a plasticising agent.

PROVENANCE AND CONDITION OF THE LEATHER

The leather comes mainly from a few large sites in the
centre of the city. The conditions are wet and
anaerobic. One Roman site alone (Copthall Avenue)
contained a layer consisting of 90% leather waste from
shoe-making. Two medieval sites (Swan Lane and
Billingsgate) also produced a great number of finds,
mainly shoes. It is assumed that the leather is
vegetable tanned but this has not been verified. The
condition of the leather itself varies greatly. Some
is remarkably good, flexible with little sign of
degradation, however other pieces can be hard, brittle
or delaminating badly. There can be considerable
concretions of soil and metal salts especially if there
are metal fittingspresent, eg hobnails. In general
medieval material is in better condition than Roman
although this is not always the case. This could be
due to a variety of factors. It may be a simple case
of the length of time of burial resulting in greater
degradation. However it may also be true that the
hob-nailed boots of the Romans lasted longer in use
than the softer shoes of medieval date and the leather
was therefore more deteriorated when buried. The
history of the material before, as well as after,
burial is important, as is the type of leather used.
A considerable number of objects have metal fittings.
Hobnails, buckles, strapends, decorative studs and
other accessories are common. Several examples of
gilded or painted leather have also been successfully
treated. In most cases these objects can be initially
treated as other leather finds.

PROCESSING AND TREATMENT

PROCESSING AND STORAGE PRIOR TO CONSERVATION

These stages are the responsibility of the finds
sections of the archaeological departments. All
leather is given a preliminary wash before storage.
Objects of particular interest (eg those that are
fairly complete, show interesting details of working
or are of an uncommon type) are accessioned individually
and drawn 1:1 prior to conservation. It is then all
stored either wet or frozen. For wet storage it is
kept in a solution of sodium orthophenyl phenate (SOPP)
fungicide in tap water in a heat-sealed polyethylene bag
with as little air as possible. If frozen it is again
kept in a heat-sealed bag but with the minimum amount
of water and air and no fungicide. A domestic chest

freezer is used (c-18°C). No damage due to freezing
has been noted. In both cases two polyethylene fibre
labels (TYVEC) are kept with each object.

All leather undergoes the complete conservation process.
Individual records are kept of the accessioned objects
only.

CONSERVATION TREATMENT

In the past various conservation methods have been
investigated (2). These have included the use of
different plasticising/lubricating agents and both
solvent and freeze-drying techniques. In summary the
following conclusions were reached:-

- Firstly, and applying the rule of "minimum inter-
vention", it is important that methods should be
chosen that result in the least chemical interference
with the leather. To this end freeze-drying techniques
would be preferred over organic solvent (acetone,
alcohol etc.) ones as the latter may extract tannins,
humates and lipids as well as possible remains of dyes
and finishes. the use of complexing agents (eg EDTA)
to remove salts and concreted soil should also be kept
to a minimum as these too may affect dye remains.
Freeze-drying is both safer for the conservator and is
less time-consuming than the use of solvents. However,
due to the initial large financial outlay necessary
for the plant it is realised that freeze-drying is
beyond the means of many laboratories.

- It would appear that plasticisers introduced into the
leather to make it more flexible should preferably be
applied before drying (the drastic step) rather than
after as a dressing. This allows for better penetration
and may reduce the possibility of bonding between
fibres.

- Of all the plasticising agents investigated (glycerol,
PEG 400. sorbitol, water soluble BAVON ASAK 520S)
glycerol consistently produced the best results, the
optimum concentration being 15-30% v/v. Higher
concentrations might result in seepage (however this
has not been investigated). This confirms results
obtained by Anthony David, who pioneered the use of
glycerol before freeze drying (3) and Jacqui Watson (4).
It is now used by many laboratories.

The conservation procedure now in use at the Museum of
London can be divided into four stages: - cleaning,
plasticising, freezing and freeze drying.

CLEANING The leather is supported throughout cleaning
on a foam-covered perspex sheet and sprayed continuously
with tap water. It is brushed with a solution of
non-ionic detergent (BRlJ 35). At this point it is
examined for traces of thread, gilding, painting etc.
Each object is then put separately in a re-usable bag
of polyethylene or polyester (TERYLENE) mesh closed
with non-rusting staples. The TYVEC labels remain with
the objects throughout conservation. The leather is
then rinsed continuously overnight to remove fungicide
and detergent. In rare cases complexing agents are
necessary to remove concretions. If so the objects are
usually soaked in a 5% solution w/v of disodium EDTA
for two hours and then rinsed thoroughly.

PLASTICISING The leather is soaked in 25% solution
w/v of glycerol for three days. One batch of solution
is used three times, however the last time is only for
unaccessioned material as by this time it is
considerably diluted. See below for discussion on the
use of glycerol. It has not been found necessary to
add a fungicide. Only one case of fungus growth after
drying has been noted.

FREEZING The objects are removed from the net bags and
excess glycerol solution is blotted off. They are then
individually packed for freezing and freeze-drying.
Most pieces can be put between two sheets of acid-free
card stapled together. These give support, prevent
distortion during drying and, to some extent, flatten
pieces were necessary. If more support is needed, or
if objects are an awkward shape, foam, bandages and
rigid sheets (PERSPEX, glass) can be used. Care must be

taken to cover an object either completely or not at all otherwise there can be migration of glycerol solution resulting in darker patches on the finished artefact. The leather is then left in a domestic chest freezer for at least 48 hours (-18°C). It can be stored thus for unlimited periods if necessary.

It is sometimes possible to freeze objects in the freeze-drier chamber if wished.

FREEZE-DRYING(5) After loading the chamber temperature of the freeze-drier is kept low for a few hours (c-20°C) to ensure the leather is completely frozen.

It is then raised to between 0 and 5°C. Drying is usually complete within 48 hours. It has not been found that the packaging inhibits the drying rate to any significant extent.

When the leather is removed it is hard and stiff due to complete desiccation. However, it quickly reaches ambient humidity and becomes softer.

AFTER DRYING

A few objects may need further flattening out. This can usually be carried out successfully without rewetting by the application of gentle sustained pressure. In some cases it may be necessary to place them in a high RH for a few hours first. Metal fittings can be cleaned further and treated accordingly.

Most objects are studied in their component parts. However it is of interest to reconstruct a few, especially shoes. For this techniques devised and reported by Elizabeth Peacock (6) are employed. Both cellulose nitrate (HMG) and polyacrylate (PLIANTEX) adhesives are used. PLIANTEX can also be applied locally as a consolidant where necessary. Dyed and waxed linen thread, dyed crepeline and brown felt are used for stitching, backing and gap-filling.

PACKAGING

Most objects can be stored in perforated polyethylene bags with an acid-free board support where necessary. It is possible in this way to see an object without removing it from its bag.

INVESTIGATIONS INTO SOME EFFECTS OF GLYCEROL AS A PLASTICISING AGENT

Experiments are still in progress into some possible effects of the use of glycerol on leather, in particular on the dimensional stability and hygroscopicity of the treated objects. In addition an investigation has been carried out to ascertain the optimum length of time for the glycerol soak. I would like to report here on our interim results.

DIMENSIONAL STABILITY AND HYGROSCOPICITY

It can be demonstrated easily that the dimensions of treated leather are affected by the concentration of glycerol solution used and maybe also by the ambient RH at which the dried pieces are stored. Table 1 records the shrinkage of samples freeze-dried from varying concentrations of glycerol. Throughout this paper shrinkages are expressed as a percentage of the wet dimensions. Final measurements were taken after the leather had reached ambient humidity (RH c50%).

| glycerol conc.	0%	10%	20%	30%
average shrinkage	6.2%	4.6%	1.7%	1.0%
shrinkage range	1.9-12%	0.7.5%	0.3.5%	0.2.1%
no. measured	11	40	6	4

Table 1.

The results obtained for 20 and 30% glycerol solutions are tentative due to the extremely small sample taken. Our standard treatment at the time (1981) used only a 10% solution. We now recommend the use of higher percentages.

It is hoped to carry out experiments in the future to ascertain the effect of different concentrations of glycerol on the dimensions of totally desiccated leather, ie leather that has just been removed from the freeze-drier, and to evaluate its subsequent behaviour when subjected to varying RHs. In this way it may be possible to establish a link between both the glycerol and water contents of the leather and its dimensions. A simple experiment has already been carried out to monitor the take-up of water from an atmosphere of high RH by leather treated with different concentrations of glycerol by recording the increases in weight of the samples.

Experimental: Samples treated with 0, 20 and 30% glycerol solutions were freeze-dried, left to reach ambient humidity (c55%) and placed in a humidity chamber at high RH (c90%) along with a sample of pure glycerol. they were weighed daily for 22 days. The glycerol sample alone was weighed for a further 26 days.

Results:

% weight gain
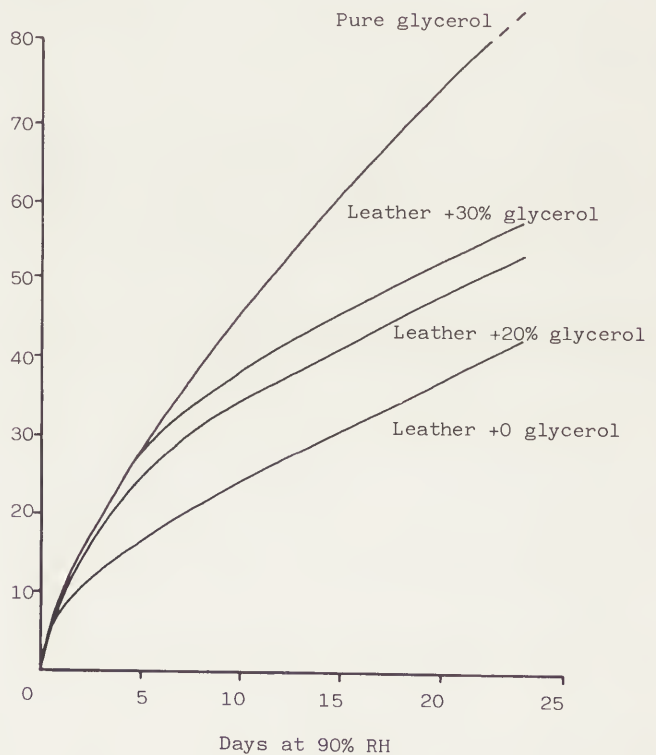
Graph 1. % weight gain with time at 90%RH

It can be seen from the graph that leather treated with glycerol shows behaviour intermediate between that of untreated leather and pure glycerol, the degree depending on the concentration of the solution used. The glycerol may, however, have a disproportionate effect compared to the amount of it we suppose to be present in the leather.

LENGTH OF TIME OF THE GLYCEROL SOAK

The length of time leather is soaked in glycerol during our standard procedure has been fairly arbitrarily set at 3 days. An experiment was carried out to see the effect of both shortening and lengthening this time. Results were assessed by recording shrinkages and weight loss during treatment. The flexibility of the dried samples was also recorded, however the monitoring of this is to a large extent subjective.

Experimental: A group of unassociated medieval shoe soles and uppers were used as these had the advantage that they could be sacrificed. Each piece could therefore be cut to provide samples as nearly identical as possible. The leather was in relatively good

condition.

The pieces were washed, weighed accurately and drawn 1:1. The flexibility when wet was noted. They were divided into 3 groups treated as follows:

Group 1 - 6 samples. Control group. No glycerol soak.
Group 2 - 18 samples. 25% glycerol for 1 day.
Group 3 - 18 samples. 25% glycerol for 5 days.

All were then frozen, freeze-dried, and allowed to reach ambient humidity (c35%). After 3 days they were reweighed then measured in 2 directions at right-angles to ascertain shrinkages. The results are recorded in Table 2. The weight loss is expressed as a percentage of the original wet weight and is the figure for the group as a whole. The shrinkage is the average for the group.

Group	Days in glycerol	% weight loss	% shrinkage
1	0	62.4	11.1
2	1	38.9	2.8
3	5	38.0	2.4

Table 2

Results: The leather not treated with glycerol (group 1) had both high weight loss and shrinkage as would be expected. It was very stiff. The weight loss and shrinkages for groups 2 and 3 were virtually identical with each other and there was no significant difference in flexibility between them. It would therefore seem that these samples reached equilibrium with the glycerol solution after only 1 day and that prolonging the soak would be unnecessary in this case. However all the leather was relatively thin. Thicker pieces may require a longer soak. Anthony David recommends considering the thickness of the leather when choosing the glycerol concentration (7). It may be necessary to vary the soak time as well.

CONCLUSIONS

- The concentration of glycerol used has a direct effect on both the hygroscopicity of the finished object and its final dimensions. However, the relationship between these two properties has yet to be established.

- In many cases it may be sufficient to soak leather for as little as 1 day.

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SORBITOL TREATMENT OF LEATHER AND SKIN:
A PRELIMINARY REPORT

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SUMMARY

To prepare dried and crushed Eskimo artifacts for
exhibition, treatments were tested that would permit
softening and reshaping while maintaining an aesthetic
appearance. Due to dependence of leather stability on
moisture content, humectants were choice systems for
testing. Sorbitol and glycerol have been character-
ized in conditions of high relative humidity. From
experimental data, sorbitol was shown to have greater
moisture regulating properties than glycerol. Two
case studies are also described.

Introduction

Eskimo artifacts of leather, skin, fur, and gut often
become stiff and brittle upon drying in many storage
environments. Methods of treatment to soften and to
restore these types of artifacts include: subjection
to high humidity;[1] soaking in water;[2] incorporation of
stabilized olein soap in emulsion form;[3] application
of lubricants such as oils,[4] fats,[5] or various dress-
ings;[6] and impregnation with humectants.[7] The goals of
these treatments are reversibility, induction of
softening to permit reshaping, lasting effect and
little to no change in original appearance. While
many of these treatments do achieve a certain amount
of flexibility in dry leather, oftentimes this flexi-
bility is accomplished at the expense of surface
appearance. Most frequently, the leather becomes
darker. Equally unsatisfactory is the "greasy"
surface or wet appearance that can accompany a condi-
tioned leather article. Therefore, several leather
treatments were tested in hopes of determining which
method would soften brittle leather, remain effective
over time and yet maintain an aesthetic appearance.

Background

The processing of hides and skins into leather is a
multi-stepped procedure. Collagen, the major protein
constituent, is converted into a stable product by
many chemical and mechanical operations. Chief among
these is the use of a tanning agent which causes a
physicochemical change in the proteins of the hide.
This change renders the skin resistant to putrifi-
cation, rotting, enzymes, and hot water; improves its
dimensional stability, abrasion resistance, resistance
to chemicals and to heat; and makes it serviceable for
long periods of time.[8] The actual chemistry involved
in tanning is beyond the scope of this paper. How-
ever, tanning in relation to ethnographic practices
has been discussed by others.[9]

As noted above, collagen is the basic component of
leather to which water is linked by chemical bonds and
by capillary attraction. Immediately after tanning,
leather contains about 60% water and after final
processing and drying the water content totals approxi-
mately 15%, varying according to tannin employed.[10]

The stability of leather is therefore dependent on the
moisture content of its environment. Below about 50%
relative humidity (RH) the chemically linked water
will be drawn out of the fiber network causing the

leather to become dry and brittle. The leather also
suffers from loss of strength and flexibility since
the fiber bundles can no longer slip easily over one
another without the lubricating moisture. When
conditions of excess moisture exist, hydrolysis of the
collagen polypeptide chains is initiated. In combin-
ation with heat and acidic conditions the process
becomes more severe and leads to denaturization and
putrification.[11]

Because regulation of moisture content is primary to
the durability of leather, the aim of conservation
treatment is to stabilize the water content of leather
and to bring it into equilibrium with its internal and
external environment. Certain materials function to
achieve this balance better than others.

Humectants are hygroscopic chemicals which produce a
stabilizing effect on the water content of the mater-
ial in which they are contained. Their action keeps
the moisture content within a narrow range during
conditions of fluctuating humidity.[12]

Glycerol (glycerin; glycyl alcohol; 1,2,3-propane-
triol) $C_3H_5(OH)_3$, a trihydric alcohol is by far the
most familiar humectant. It is a clear, colorless,
odorless, syrupy liquid which is soluble in water and
alcohol. Glycerol has a slightly sweet taste and is
used as a lubricant, softener, bacteriostat, pene-
trant, emulsifying agent, tobacco conditioner, plasti-
cizer, and in liqueurs, cosmetics and antifreeze
mixes.[13]

Sorbitol (D-sorbite; D-sorbitol) $C_6H_8(OH)_6$, a hexa-
hydric alcohol, is a white, odorless, crystalline
powder. It is soluble in water, glycerol, propylene
glycol and slightly soluble in methanol and ethanol.
Sorbitol has a faint sweet taste and is used as a
moisture conditioner in cosmetics, bodying agent,
softener for candy, plasticizer, sweetener, emulsi-
fier, thickener, and surfactant.[14]

Stambolov reported that while both of these humectants
behave similarly, sorbitol appears to have much better
moisture regulating properties.[15] In high humidities
glycerol absorbs twice as much water as sorbitol.
This effect might account for the wet, greasy feel
often associated with objects previously treated with
glycerol and stored in areas with fluctuating relative
humidity. (Probably for this reason conservators have
been advised not to use hygroscopic materials in the
treatment of deteriorated leather if the storage
environment is not air conditioned.[16]) In addition,
Stambolov stated that sorbitol retains its moisture
for longer periods than glycerol as the RH decreases
and attains equilibrium more rapidly than glycerol
with increasing RH.[17]

Considering the evidence presented by Stambolov, it
became apparent that sorbitol impregnation was a
system worthy of further testing and investigation.
As early as 1938[18] it was noted that sorbitol exhi-
bited superior properties to glycerol as a humectant
for a variety of materials. However, the use of
sorbitol in conservation treatments has been discussed
very infrequently.

The use of sorbitol on gilt leather as both a swelling
agent and as an ingredient in an oil-emulsion lubri-
cant are described by Stambolov with very positive
results.[19] Hallebeek and Van Soest[20] as well as
Ganiaris, Keene and Starling[21] incorporated sorbitol
into their comparative treatment tests. It is hoped
that this presentation will give an awareness of the
practical use of sorbitol to other conservators faced
with treating ethnographic artifacts of skin, fur, gut
and similar substances and provide yet another system
for consideration.

Experimental

Comparative tests were conducted both quantitatively,
procedure 1, and subjectively, procedure 2. Percent
weight gain of various samples treated with glycerol
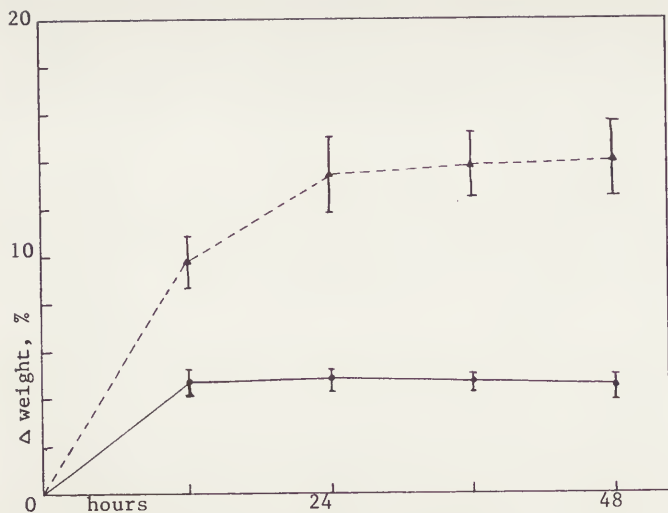and sorbitol was measured over time. A second set of

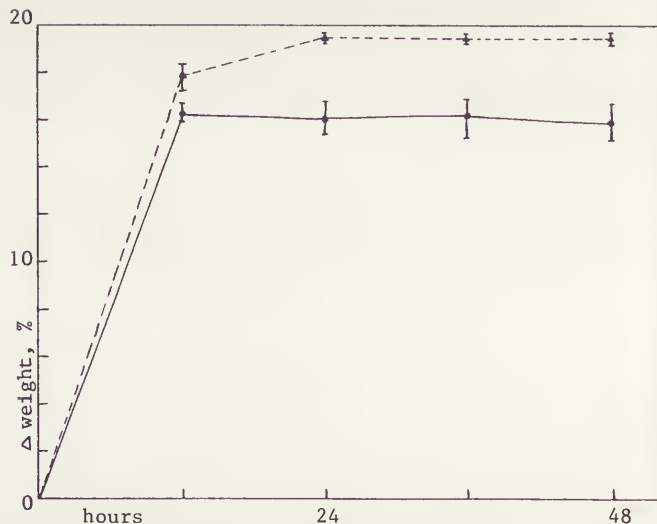Figure 1: Leather Samples, 80% RH 25°C
(after 36 hrs at 40% RH 25°C)

Figure 3: Aged Leather samples, 80% RH 25°C
(after 36 hrs at 100°C)

(In figures 1-4, --▲--- = glycerol, —●— = sorbitol)
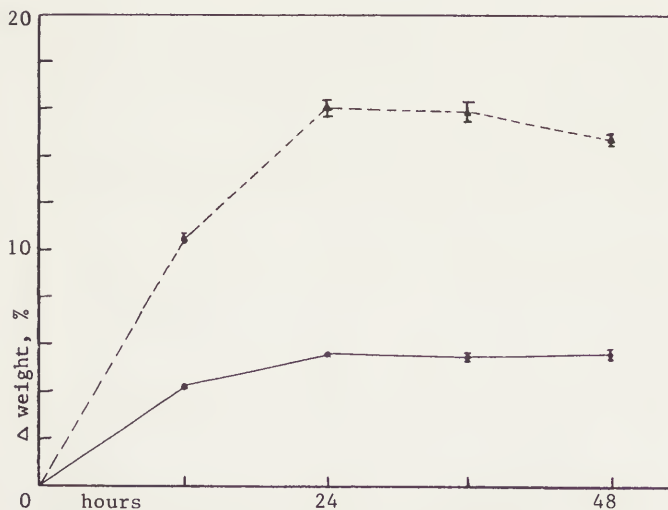

Figure 2: Sheepskin samples, 80% RH 25°C
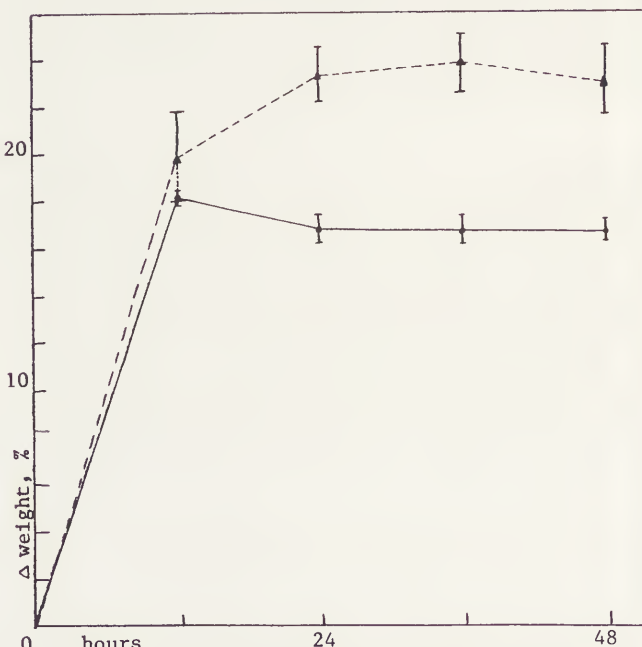(after 36 hrs at 40% RH 25°C)

Figure 4: Aged Sheepskin samples, 80% RH 25°C
(after 36 hrs at 100°C)

samples judged flexibility and surface appearance
following selected treatments.

Procedure 1: Samples of modern tanned leather and
sheepskin were saturated with 25% glycerol in ethanol
or 5% sorbitol in ethanol:water, 1:1, and allowed to
air dry. Once wetted in either solution the samples
became very supple. One-third of the samples were
first aged at 100°C for 36 hours prior to subjection
to high humidity conditions of 80% RH and 25°C for 48
hours. Another third were initially subjected to 40%
humidity at 25°C for 36 hours before raising the
humidity to 80% at 25°C for 48 hours. The third set
of samples was maintained at constant conditions of
50% RH and 21°C. Samples were weighed at 12 hour
intervals and these measurements were calculated for
mean and deviation from the mean, using duplicates.

Results: (Refer to Figures 1-4) Leather and sheepskin
samples were placed at 80% RH 25°C after an initial 36
hour incubation at 40% RH and 25°C (Figures 1 and 2).
At first all samples gained weight due to moisture
absorption from the humid environment. However,
sorbitol- treated samples of leather and sheepskin
established equilibrium thereafter while the glycerol-
treated samples continued to absorb water before
establishing equilibrium. The percent weight gain of

glycerol- treated samples was more than double that of
sorbitol treated samples for both skin and leather.
In Figure 3, leather samples were placed at 80% RH
25°C, after simulated aging at 100°C for 36 hours.
The sorbitol-treated samples established equilibrium
immediately after initial moisture absorption while
the glycerol-treated ones continued to gain weight
before establishing equilibrium. Sheepskin samples,
after similar simulated aging, were placed at 80% RH
25°C (Figure 4). In both glycerol and sorbitol-
treated samples there was a rapid initial percent
weight gain. While the glycerol-treated samples
continued to gain weight before establishing equili-
brium, the sorbitol-treated ones actually lost mois-
ture to establish equilibrium. Comparison of the data
suggested that the aged sorbitol-treated samples of
leather and sheepskin (Figures 3 and 4) equilibrate at
approximately the same percentage of weight gain,
whereas the aged glycerol-treated samples did not
correlate.

In addition to these measured results, striking
subjective differences were noted. After heating at
100°C for 36 hours the glycerol-treated sheepskin was
curled and very stiff. In fact, the glycerol-treated
samples were brittle and cracked on manipulation. In
contrast, the sorbitol-treated sheepskin was straight

and exhibited some flexibility. Upon humidification, the glycerol-treated sheepskin regained its flexibility but retained its curled position and remained darker. The sorbitol-treated sheepskin was very flexible and exhibited no change in appearance. Heating of the leather samples induced stiffening on all accounts. In addition, glycerol-treated leather was very dark with a greasy appearance. High humidity increased the flexibility of the samples; sorbitol-treated leather was not detectable while glycerol-treated leather became very dark. For those samples first subjected to 36 hours at 40% RH, the glycerol-treated sheepskin and leather were dark and clammy to the touch. Sorbitol-treated samples remained virtually unchanged with respect to color, feel, and flexibility in the different humidity conditions.

Discussion: As demonstrated in Figures 1-4, sorbitol appears to have strikingly better moisture regulating properties than glycerol. Sorbitol confines the moisture intake to a much narrower range than the corresponding glycerol-treated samples. When coupling this data with the flexibility attained and retention of original appearance, these preliminary findings suggest that sorbitol appears to be a more satisfactory humectant than glycerol for the systems tested.[22] Experiments are in progress to determine the action of glycerol and sorbitol in fluctuating environmental conditions and to test for effectiveness over time.

Procedure 2: In order to simulate old, dried, crushed skin artifacts, fur samples were moistened, folded, clipped into position and heated for one week. Upon removal from the heating cabinet the samples were stiff, hard, and retained the fold lines when unclipped. These prepared samples were treated using a selection of agents that would soften the material and enhance reshaping, in this case unfolding and flattening. The samples were saturated with the softening agent, placed between blotters, weighted flat, and dried in the air.

Results: The five softening agents tested gave the following results:

1. Humidification to 85% RH - sample not softened sufficiently to reshape, some stiffening after drying, no color change.

2. Bavon ASAK ABP, 5% in varsol - some flexibility after 5 hours, sample very greasy when wet, did not retain new position fully, smelled of solvent, no color change.

3. Sorbitol, 3% in ethanol:water, 1:1 - extremely flexible within 1 hour, easily reshaped, retained new position on drying with some loss of flexibility, no color change.

4. British Museum Leather Dressing - gained some flexibility, could not fully reshape, surface darkened and was slightly tacky.

5. Glycerol, 25% in ethanol - extremely flexible within 1 hour but greasy surface, easily reshaped, retained new position on drying with some loss of flexibility, color darker than original.

Discussion: These subjective tests clearly indicated that sorbitol impregnation allowed the samples to be totally reshaped without any change in surface appearance or texture.

Based on all the above experimental data, sorbitol was chosen as the softening and reshaping agent in the treatment of dried and crushed Eskimo artifacts described below in the case studies.

Case Studies

Shortly after the purchase of the Alaskan Territory from Russia, Edward W. Nelson was sent by the Smithsonian Institution to St. Michael, Alaska and the northern coast of Siberia from the years 1877-81. During that time, Nelson collected products of Eskimo handicraft while continually observing and inquiring about the habits, customs, beliefs, regulations and ceremonies of the various tribes. The manuscript of his research and acquisition projects, illustrated with examples from the ethnologic specimens he collected, was published in 1899 as the Eighteenth Annual Report of the Bureau of American Ethnology (BAE). Due to Nelson's excellent work we are fortunate to have gained a memoir that describes the relationship the Bering Strait Eskimo had with their environment and its influence over every aspect of their lives before conspicuous changes occurred following contact with the non-indigenous American cultures. The Nelson collection of over 10,000 artifacts is unsurpassed in richness and variety.[23]

In preparation for the exhibition, "Inua: Spirit World of the Bering Sea Eskimo," at the National Museum of Natural History, Smithsonian Institution, several of the specimens collected by Nelson required conservation treatment. Two artifacts were restored close to their original appearance with the use of sorbitol, details of which follow.

Wolverine Tool Bag, Cape Darby, Alaska (48.089)

The tool bag is composed of wolverine skin and seal skin sewn together with sinew thread. A walrus ivory handle is attached with rawhide. The overall condition of the tool bag as received was fair. The wolverine skin sides were completely crushed into the seal skin base and retained no original contour. There was little flexibility and no way to stuff the bag back into proper shape without first softening the skins. Hairs were also falling from the skin. The seal skin base was stiffer than the wolverine skin and also very distorted. Numerous tears and a hole were present on the base.

The first step of the softening treatment was to place the bag on a layer of towels wetted with 3% sorbitol, ethanol:water, 1:1, to which several drops of 2% thymol in methanol were added. A polyethylene liner was placed only on the base inside the bag to protect the hair side of the seal skin. Sorbitol wetted towels were then carefully placed along the interior walls of the bag. These were then isolated with polyethylene liners and the bag stuffed out with dry towels and bubble-pack. The entire bag was then covered with polyethylene. Periodic checks were made to test flexibility of the skins and record any changes. After three hours of marinating in the sorbitol, the skins were very workable. All stuffing, wet towels and polyethylene were removed from the interior and exterior. Clean, dry towels were placed inside and the bag was weighted on the interior of the base. The sides and walls were stuffed out so that the bag would dry in a natural looking, slightly open position. The bag air dried for several days with numerous changes of the towels and frequent checks for any disturbing changes. No changes were noted and the skins remained the same color upon drying. Following repair of the holes in the base and brushing of the furs, the treatment was completed having restored the bag to much of its original appearance and to an exhibitable condition.

Gutskin Parka, Kamlayka, Golovina Bay, Alaska (43.335)

The gutskin parka is composed of seal intestine sewn together in coiled rows with very small stitches of sinew thread. The parka is decorated with small pieces of feather and red wool fiber sewn at intervals all along the horizontal seams. A one-inch strip of fur is sewn along the entire bottom edge of the parka.

The intestinal material was totally crushed and wrinkled when received for treatment. It was weakened and cracked in some places and only partially flexible. Several tears both on and off seams were present. The strip of fur along the bottom was also dry and inflexible. It was bent out of shape and plane in many locations. The feathers were stable;

however, some had been bent out of proper position.

Initial treatment was to lightly mist the front and back surfaces of the parka with distilled water. As the intestinal materials began to gain flexibility due to the moisture, towels moistened with 1½% sorbitol in water:ethanol, 2:1, to which several drops of 2% thymol in methanol had been added, were placed on the inner surfaces of the parka. Stuffing materials were gently eased into the parka with care taken to retain an "authentic looking" shape without overstuffing. The parka was then covered with polyethylene. The sorbitol wetted towels were removed after two hours marination and replaced with dry towels and poly- ethylene stuffing. The fur strip along the bottom was weighted between sorbitol moistened towels. After two hours, the wet towels were replaced with dry ones. The fur strip could be eased into proper position due to its gained flexibility and was allowed to dry under weights. Some areas of the fur required a second treatment with sorbitol to remove bends and kinks. Misaligned feathers were wetted and lightly weighted to dry in proper position. After air drying, the parka was cleaned and holes and tears mended. The polyethylene stuffing was replaced with acid free tissue until properly padded exhibition supports were contructed. Again, no changes were noted in color or transparency of the materials.

Conclusions

The evidence presented here, together with that earlier described by Stambolov and members of his laboratory staff, should encourage conservators to include sorbitol in their tests and future treatments of leather, skin and gut artifacts which require softening and reshaping. Although not suitable for all ethnographic materials of skin products, case studies and experiments have shown that soribtol does have unique properties of value to the preservation and conservation treatment of leather-related pro- ducts. The most important considerations for the continued preservation of leather is to ensure proper environmental conditions; maintenance of relative humdity between 50-70%, provision of good ventilation free of dirt, dust and pollution, and avoidance of direct contact with heat and moisture.

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CONSERVATION OF ARCHAEOLOGICAL LEATHER (ON
THE BASIS OF ARCHAEOLOGICAL DATA OBTAINED
IN TARTU AND IN TALLINN IN 1981-1982)

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SUMMARY

The leather articles found during archaeolo-
gical excavations in Tartu and in Tallinn in
1981-1982 are of great historical importance.
They add considerable information to our
knowledge in the handicraft of the 11th-14th
centuries in Estonia, and as well in the
character of trade relations with other towns
of the Hanseatic League.
Conservation of archaeological leather artic-
le finds includes their simultaneous measur-
ring, photographing and making the technical
drawings. The articles should also be examin-
ed from the point of view of history of art,
i. e. their production methods, ornamenting
and material should be determined. Complex
researches in the leather article finds help
to date the finds and to avoid mistakes in
conservation (deformation etc).
For conserving leather article finds the me-
thod by B. Mühlethaler, i. e. conservation
by the means of polyethylenglycol has been
applied.
The results of the work are the following
ones: conservation of leather details, attri-
bution of articles and suggestions for recon-
struction.

Archaeological excavations in Tartu (Dorpat)
and in Tallinn (Revel) in 1981-1982 were ex-
ceptionally rich in leather article finds.
177 leather details from Tartu finds - mainly
parts of footwear and production remnants -
were conserved. The excavations took place at
Tartu Town Hall square and in its immediate
vicinity in connection with the setting of an
heat track in the old part of the twon. In
the hollow of the track constructions of an
old log building were found and using radio-
active carbon C^{14}(TA-1429) dated to 1200±40
years by A. Liiva and T. Rinne, senior rese-
arch workers of the Institute of Botany and
Zoology of the Estonian Academy of Sciences.
From the culture layer near the wooden build-
ing numerous details of leather articles and
leather processing remnants were also unear-
thed. Leather details were found up to the
depth of 240 cm. They were quite well pre-
served, partly due to the vicinity of the
Emajogi River (300-500 m).
Archaeological excavations in Tallinn, in Va-
na Tooma street N 5 were carried out in con-
nection with the building of a trade centre
in the central part of the old town. In this
area sites of medieval cattle-sheds and an
old town well were found. In addition to pot-
tery and wooden bontainers numerous details
of footwear, cold steel sheaths and pouches
were unerthed. The total number of the deta-
ils was 160.
Archaeological leather needs immediate con-
servation in order to preserve the natural
shape of the found articles and to understand
the relations between separate details. To
preserve maximum information, about 330 lea-
ther article details + production remnants
had to bedealt with immediatela and profici-

ently. The conservation work was carried out
by the restoration department of the Estonian
State Art Museum. The staff of this depart-
ment was experienced in the conservation of
medieval leather bindings and furniture cove-
red with leather.
The restorers and chemists had to do with se-
veral problems needing quick and complex so-
lution. The conservation method is chosed de-
pending on the preservation stage of an ar -
ticle, on its material and ornamenting tech-
nique. The conservation work was also compli-
cated due to the danger that leather details
would lose too much of their original humidi-
ty and deform as a result of this process,
and also due to the fact that only little is
known about the medieval footwear production
techniques.
The main damages of the leather finds:
1) mechanical; earth and clay marks;
2) separation of tannin from the material (le-
ather;
3) absorption of soil salts in the leather
and their crystallization, resulting in a
bluish-green precipitation on the leather
surface;
4) corrosion due to the metal supplements
(nails, buckles);
5) biological contamination.

Green precipitation was determined by H. Vii-
ding, Master of geological-mineralogical sci-
ences as vivianite.
The water content of unearthed leather is abo-
ut 80%, its outward appearance - the surface
structure of leather and the shape of an ar-
ticle - has often preserved, but under diffe-
rent conditions - open air, wind, sunlight -
it undergoes active changes. Without immedia-
te conserving treatment leather becomes dry
and brittle, the surface crackles, leather be-
comes stratified and the deformation of an
article and details occurs. Leather may pe-
rish and it is impossible to restore it.
This is the reason why archaeologists have
tried to find possibilities for immediate con-
servation of leather at excavation sites. For
this gelantine, varnish, plaster, paraffin
and wax have been used.
Owing to the further developments in chemical
sciences high-molecular compounds are being
applied also in the field of archaeology. Us-
ing the B. Mühlethaler's method liquefying
polyethylenglycol 1000 was applied for the
first time in our practice and it proved to
be suitable for conservation of wet archaeolo-
gical leather.
After mechanical cleaning all the details were
measured, drawn and photographed. Tables con-
cerning the soles and the upper details of
footwear were composed. By the means of a mic-
roscope types of leather were determined on
the basis of leather surface structure and di-
sposition of hairs.
The visual and statistic analyses of leather
details and the comparison with the finds at
archaeological excavations belonging to the
same period in Lübeck led to the following re-
sults:

Type of leather	Tartu 11-15th c.	Tallin 14-16th c	Lübeck 13-14th c.
horned cattle skins	48%	82%	47%
goat-andsheep-skins	12%	4%	28%
pigskins	-	-	19%
bearskins[x]	30%	-	-
calfskins	10%	14%	6%

[x] Bearskin formed 85% of the upper leather of
footwear.

First and foremost we are interested in the
age of the finds. Here we can use the data
concerning the other finds at the same depth.
In Tartu the age of the logs was determined
using dendrological method. The age of the

logs is 750±40 years. A number of comparison
materials made it possible to date the potte-
ry etc. The high percentage of bearskin in
the finds of Tartu points to the period when
the bear as the most dangerous carnivore in
our woods was intensly hunted in order to
protect cattle. We can also use the resear-
ches based on bone finds and showing the dis-
tribution of the Bear (Ursus arctos) etc.
The footwear finds in Tartu included three
leather details with dugs (NB 579, TRV-82
R-2-311, TRV-8 R7/8-300, TRV-82 R2/31), be-
longing to the bear (zooloogist M. Kaal).
Skin structure, thickness (2.3-3.5 mm), the
distribution of hair terminals and the hair
measures confirm this opinion. As a conclu-
sion we can state that the abundance of be-
arkin indicates the local origin of the foot-
wear.
For determination of the age of the footwear
we can use the data on the types of footwear,
determination of production techniques on the
basis of stitching holes existent on the de-
tails and also the number and the construc-
tion of the details used in footwear produc-
tion.
Cold steel sheaths are relatively numerous in
the finds in Tallinn, for knives, daggers and
swords needed leather covering. The sheaths
are often decorated. Among Tartu finds the
most frequent ornamenting techniques are
                      and notching, in Tallinn finds
composing of different leyther types (calf-
 skin+goatskin), frazzling, ornamenting with
leather twining and tassels. But the most
exact dating becomes possible owing to blind
print - the imprints of metal stamps are used
to form a pattern. A knife sheath and a sword
sheath (N:20,21 RVR) are decorated using this
technique, the ornamental motifs are ab an-
chor and a twining motif in a rhomb. One im-
print is figural - a lion on a square. The
stamp imprints are in the positive relief and
this indicates that they go back to the 15th
century for all the earlier imprints were
carried out in the negative relief. The out-
ward shape of the stamps - rhom and square -
confirm the opinion that they belong to the
14th-15th centuries for at that time the
rhombic and horizontal composition was domi-
nating in the binding. On the basis of the
comparison of stamp imprints it is possible
to determine even more exactly the making
and time of the cold steel sheath finds.
Determining the leather finds in Tartu as go-
ing back approximately to the 11th-14th c.
and in Tallinn to the 14th-16th c. we shall
examine the comparative data for the same pe-
riod in archivals. We tried to make clear the
handicraft specialities of the citizens   of
Tallinn on the basis of the data in "Revaler
Bürgerbuch" 1409-1624, but on several occa-
sions it is inadequate for not all the names
of people registered as citizens were follow-
ed by the registration of their speciality.
When comparing several archivals we obtained
the following data concerning leather arti-
sans in Tallinn in the 14th century:
leather tanners - 7   saddlers - 11
shoemakers - 111   pouch makers - 2
wooden shoe makers - 2 strap makers - 9
furriers - 47   belt makers - 9
In order to explain the abundancy of knife
and sword sheaths among the archeological
finds in the Vana Tooma street we shall also
mention the numbers of swordmakers (14) and
knife makers (12) who worked here.
When comparing separate specialities we can
see that the number of the artisant connected
with leather processing is quite large. But
it still seems that the list of tanners does
not represent the real number of tanners, for
to prevent epidemics, it was prohibited for
tanners to work in towns. As fresh water is
inevitable in tanning tanners often went away
from the coastal areas. The number of furri-
ers indicates that furs were widely used as

a material for clothes.
Beside footwear the cold steel sheaths - kni-
fe sheaths, dagger sheaths and sword sheaths
form the most numerous group of articles.
The third group includes belts, purses, pou-
ches, leather gloves and sebrak. In sword
sheaths and belts blind print technique was
used but in knife sheaths and dagger sheaths
we can find frazzling, notching and metal in-
lay, Lapta balls found in the course of exca-
vations in Tartu were made of reversed calfs-
kin and filled with sheep's wool. Analogical
leather balls were found also in Novgorod,
where lapta was very popular in the 10th-14th
centuries.
In order to determine the leather footwear
 production methods and the place of the de-
tails in the footwear construction it was ne-
cessary to take into account all the leather
finds in the neighbouring countries, especial-
ly those in the towns belonging to the Hanse-
atic League.
On the baisis of special literature it was
possible to find parallels with the archaeo-
logical leather finds at Ladoga (G. S. Lebe-
dev), in Novgorod (S. A. Izjumova), in Poland
(H. Wilak), in Copenhagen (M. Hald), in Lü-
beck, Amsterdam, Haithabu (W. Groenman - van
Waateringe, A. Falk, K.-D. Hahn), in Oslo (F.
Schia), in Lund (R. Blomqvist, A. W. Märten-
son) in Helsinki (L. Tomantera), and in Lat-
via (V. Bebre). As a result of the systemizing
and comparison of our footwear details, the
author made up a scheme of footwear develop-
ment, giving a survey on the analogies and lo
cal peculiarities (at the end of the article).
For example the bearskin uppers and production
remnants found in Tartu were of double skin,
that means, the skins were duplicated before
cutting out the upper details. The upper
strap holes of a thong-boot with two straps
found in Tartu were circular, but the lower
ones were elongated, split-shaped.
There were three main types of footwear:
1. Calfsking (6-7 cm high), like a peasant
sandal
2. Seifsko (8-13 cm high) closed with 1-2
straps
3. Thong-boot (14-25 cm high) closed with 4-5
straps.
In order to avoid mistakes in conservation -
deformation of details and their separation
from the whole, it was necessary to come to
know footwear types and their designing me-
thods.
We tried to put the archaeological leather
finds into a conservating liquid before they
became dry. To keep the synthetic wax uniform-
ly warm a twofold container was constructed.
In the outer dish there was uniformly hot wa-
ter (40-60°C), but in the inner container the-
re was polyethylenglycol 1000. A marble slab
was put on the leather to keep it steadily co-
vered with liquid.
The aqueous solution of polyethylenglycol
1000:
Polyethylenglycol 1000-3000 g
Distilled water - 3000 g
Katapin -   25 g
The duration of conservation is 8-10 weeks,
after that the leather is taken out of the
liquid at the temperature of 60-65°C to remo-
ve the residues of the synthetic wax. Plane
leather can be dried between wooden shields.
The ornamented details should be treated with
special care, for the leather there is drying
in different ways, depending on decorating
techniques. So the leather details ornamented
using blind techniques should not be dried
under great weight, for it flattens the lea-
ther relief. The details with long cuts and
notches also need great care. If it is neces-
sary to restore the original shape of foot-
wear then the details should be kept in the
solution of polyethylenglycol up to their
full saturation. The saturation depends on va-

porization conditions (relative humidity in
 the room etc.). In the course of practical
work the author also noticed that the leather
details drying with their surface to the bo-
ard were less deformed than the ones in the
reverse position.
The conservation by the means of polyethylen-
glycol wax is suitable for wet archaeologi-
cal leather, it preserves the natural struc-
ture of the leather and the needed shape -
keeping in mind the museum exposition requi-
rements. The drawings made already in the co-
urse of conservation process enable us to
show the connections between separate details.
Afterwards it is more difficult to put flat
details together, the once double details can
be also more easily determined immediately
after their unearthing.
Polyethylenglycol is also suitable for con-
servation of especially brittle leather de-
tails (clothes) in the field conditions.

Keskaja nahkjalatsi tüpoloogia — P.Valk-Falk
Die Entwicklung der Schuhmode in Mittelalter
СХЕМА развития средневековой кожаной обуви

ühesoaline jalats — одночастная обувь

WEDELSPANG MOSE Nr 11408 c   SCHLESVIG   ETNOGRAAFILINE JALATS – IIRI, ŠOTI, ISLAND

WEDELSPANG, SCHLESWIG   BALLYMACOMB, INGLISE   EESTI, VORMSI, NORD MUS STOKHOLM n: 14-5296
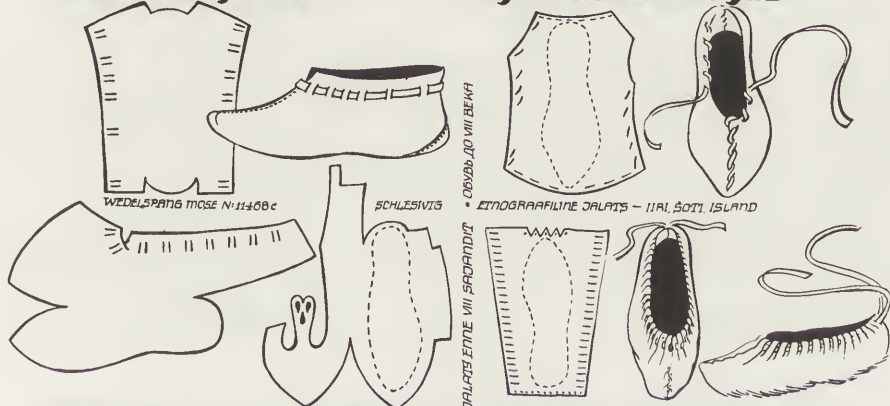
mitmeosaline ümbertöötatud jalats · многочастная обувь

BERGEN, 1300   ROOTSI, STOKHOLM   STAVKIRKE 1250   TARTU '82, TRASS II, KORRIS I № 213, hAEV. TLN 4061-2632

LÜÜBEK, XIII-XV SADAND   ROOTSI, XI SAJ.   TALLINN '82, VANA-TOOMA m.5 №3

AMSTERDAM, 1300-1400   TARTU '82, RAEKODA VÄLJAK, TRASS III

84.18.28

A COMPARATIVE INVESTIGATION OF METHODS FOR THE CONSOLIDATION OF WET ARCHAEOLOGICAL LEATHER. APPLICATION OF A PEG-IMPREGNATION TO A SHOE FROM THE 13TH CENTURY

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SUMMARY

Different methods for the impregnation of wet archaeological leather were compared. These methods, already described by different authors, were compared with new-ones, involving impregnation with water-soluble silicon monomers mixed with a plasticizer, followed by in-situ polymerization. The best results were clearly obtained through impregnation with PEG 400 and with a mixture of Polyviol and glycerine. We preferred the former for its lower hygroscopicity. This methodology was applied to a shoe from the 13th century. The shoe was impregnated for 7 weeks in 50% PEG 400, freeze-dried for 24h and conditionned at 55% relative humidity and 21°C for several weeks: the water-uptake was 18% of its weight after lyophilization. The leather was supple and its colour turned from black, before treatment, to deep brown. Impregnation with silicon monomers might be fruitful for the treatment of very deteriorated leather; a plasticizer must be added to introduce enough suppleness into the tridimensional silicon polymer.

Introduction

Most impregnating techniques can be divided into four main groups:
- the use of polyethylene glycols (PEG): one or more grades with an upper limit of molecular weght 1500; the impregnation is eventually followed by lyophilization and finishing techniques (1,2, references in 3)
- other synthetic polymers, mixed with plasticizers and/or small hygroscopic molecules; e.g. glycerine, PEG 400 (4-6)
- application of a finishing product (fatliquor, dressing), after thorough cleaning (7)
- replacement of water by a less polar solvent (3)

Often, a particular technique proved unsatisfactory in the hands of somebody else. This was probably due to both specific skill, required for any technique, and to the different degrees of degradation of the leather objects. Therefore, we have tried out different treatments on small pieces of leather in the same condition. In addition, we describe some preliminary investigations on the impregnation of wet archaeological leather with water-soluble silicon monomers, followed by in-situ polymerization.

Materials, experimental

Leather: leather samples were collected at Pommeroeul, near Mons, Belgium, where port facilities of Roman origin from the 2nd century were discovered (8).

Cleaning: two methods were compared: soaking in 1% EDTA (ethylene diaminetetraacetic acid, di-sodium salt) and sonication for a short time (described by different authors), and oxidation by $KMnO_4$, followed by reduction and acidification (9). Blanks were soaked in water. Cross-sections were analyzed for the presence of Si, Fe and Ca by X-ray fluorescence.

Water-soluble silicon monomers for impregnation and in-situ polymerization: the monomers used were 3-aminopropyltriethoxysilane (Ta) and glycidoxypropyltrimethoxysilane (Tg), both purchased from Aldrich Europe, Belgium. To reach a satisfactory rubbery state, PEG 400 was added as a plasticizer. Since polymerization must be avoided during impregnation, the leather was first soaked in denatured ethanol (3 times 24h). The impregnations were carried out in beakers, covered with double Parafilm (American Can Company). Previous gas chromatographic analyses had proved that small amounts of water did not initiate the polymerization reaction; the ethanol present in each impregnation medium certainly establishes an equilibrium in favour of the monomers. A survey of the silicon impregnations is given in table 1. Fresh media were prepared after 20 days. Water was added after 35 days. At day 46 the samples were rinsed under running tap water, dipped in deionized water and placed in a closed container at 83% relative humidity and 21°C. The dimensions of the samples were checked.

Table 1: impregnations with silicon monomers

monomer	volume (ml)	volume PEG400 (ml)	volume ethanol (ml)
Ta	40	4	40
Ta	40	6	40
Ta	40	8	40
Tg	40	8	40

Other impregnation media are described in table 2: in all mixtures but L/PEG 400, ethanol was added to conform to the silicon media. The time of impregnation was 46 days and the media were not renewed.

Table 2: impregnations, other than silicone

description of the mixture	ref.
L/PEG 400: 4g Luviskol K30 (BASF) + 6.4g PEG 400, diluted to 80 ml with water	(5)
P/glycerine: 2g Polyviol 02/270 (Belgo-labo) + 32 ml glycerine + 8 ml ethanol, diluted to 88 ml with water	(4)
PEG 400: 40 ml Polydiol 400 (Hüls) + 20 ml water + 20 ml ethanol	in(3)
Blank: 40 ml Water + 40 ml ethanol	

Further treatment of all leather samples: after impregnation, each sample was cut in two pieces, (a) and (b). The (a) pieces were packed airtight in plastic bags, frozen at -30°C for 1h, freed from the plastic and lyophilized at room temperature and at 0.02 mm Hg, for 24h. The freeze-dried samples were conditionned at 55% relative humidity and 21°C, for 2 days before their dimensions were checked. The (b) pieces were not lyophilized, but conditionned in a similar way. They were checked for suppleness and later on, dried in a vacuum exicator over silicagel and NaOH, to establish the moisture content.

Treatment of a shoe from the 13th century, excavated near "Lahamaide", region of Ath, Belgium:

The excavated shoe, largely held together by the clod of earth in which it was brought to us, was kept in water at 5°C over a long period. The addition of some thymol crystals prevented microbial growth. When the shoe was cleaned with fresh water and by careful brushing, it fell apart in four main pieces: the sole and one main and two minor upper pieces. Sticking earth and some metal deposits were removed with a scalpel. All pieces were soaked in 1% EDTA for 2h, followed by short sonication in the same medium. The EDTA solution was removed and the leather was rinsed under running tap water for 6h.

Microscopic observations revealed a thorough cleaning of the pores.
Impregnation occurred at room temperature in a glass vessel containing 1l deionized water, 1l denatured ethanol and 2l PEG 400 (Polydiol 400 from Hüls, BRD). The vessel was covered with a glass plate. After 47 days, all pieces were superficially wiped with absorbing paper and put in a controlled atmosphere (75% rel. humidity, 21°C). The main upper part was fixed around a support, cut from 5 cm thick poly-styrene. Remaining cavities were filled with a polyester wadding. Loosening parts were kept together with gauze bandages. The sole was severely folded in one place. When still thoroughly wet, this fold could be gradually flattened with the fingers; the flattened sole was put between two stiff wire gauzes, that were clamped together. All leather parts were frozen at -195°C in liquid air and lyophilized Temperature and pressure were checked at regular intervals. The freeze-drying process was obviously finished after 24h in a mean vacuum of 0.05 mm Hg. During the last hours of this process, the shoe was slowly warmed up to 30°C. The freeze-dried leather was conditionned at 55% relative humidity and 21°C for several days. Regularly, the weight of the main part was determined. Since most of the original stitch-holes were teared, the leather parts were glued together with a cellulose glue (Tylose from Hoechst). Where necessary, loosened parts were recombined via inside lining with Japanese paper. The latest was meant to break before the aged leather, if any stretching would occur (10). Finally, the shoe was filled up with a sponge-like material in polyester, wrapped in linen.

Results:

Cleaning: from X-ray fluorescence measurements it was obvious that a more thorough cleaning was obtained with EDTA, with respect to Si and Fe; both treatments were rather unsatisfactory for the removal of Ca.

Impregnation: the experimental results are compiled in table 3. The sum of the sides of each sample, before and after treatment, allowed the calculation of the % shrinkage. The moisture content is the difference in weight of samples conditionned at 0% and at 55% relative humidity and 21°C.

Table 3: evaluation of impregnations after
         lyophilization and conditionning
         (*: LS= linear shrinkage; MC=
         moisture content)

treatment	LS(%)*	MC(%)*	evaluation
Ta/PEG400(40/4)	8	12	-brown colour, dry
Ta/PEG400(40/6)	5	11	to the touch,
Ta/PEG400(40/8)	6	11	ability to ply
Tg/PEG400(40/8)	3	7	increases with
			PEG content
L/PEG400	9	13	-black, hard, not
			plyable
P/glycerine	8	18	-black, humid
			touch, plyable
			over 180°
PEG400	3	15	-black, supple,
			plyable over 90°
Blank	15	16	-black, hard,
			brittle, curled

The best results were clearly obtained by
the impregnations with P/glycerine and with
PEG 400. The higher hygroscopicity of glyceri-
ne caused a higher moisture content and, hence
a more or less humid touch. Since too high a
water content must be avoided to prevent
microbial growth, the impregnation with PEG
400 became our method of choice.
Except in the cases where the leather was
completely hardened, lyophilization improved
its suppleness. To avoid dammage by inadequate
freezing (i.e. removal of water under reduced
pressure by cooking rather than sublimation),
a sufficiently low temperature must be
reached to freeze the impregnated leather.
Freezing at -195°C of the treated shoe did
not cause any dammage to the leather, but
manipulation of the frozen objects must be
limited: freezing was best done in a plastic
basket that could be transferred as such to
the lyophilization device.
After two weeks of conditionning at 55% relat.
humidity and 21°C, the shoe had gained 18%
of its weight after lyophilization. This
water uptake was favourable for its suppleness.
This suppleness could even be improved by
rubbing in with the fingers some Polydiol 600
wax (Hüls). We preferred this PEG since a lot
of the usual finishing products are incompati-
ble with PEG (Hüls leaflet). The only drawback
of this treatment was the dark brown to black
colour, the leather got again.
The impregnation with silicon monomers,
followed by in-situ polymerization, proved
promising if more suitable ratios of polymer
to plasticizer should be applied. However,
impregnations with these silicones might

suffer from difficulties in removing them
from the leather later on for any reason.
Although the polymers too are water-soluble,
chemical reactions between the reactive
epoxide group in Tg or, to a lesser extent the
amine group in Ta, and the tanned collagen
fibres of the leather, could render them
insoluble. On the other hand, just these
possible chemical reactions may serve to give
extra support to very deteriorated leather.
Further research in this field will be done.

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Section 19

Easel Paintings

Peintures de chevalet

FROM HANDCRAFT TO MASS PRODUCTION: NOTES ON THE MANUFACTURE OF OIL PAINTING MATERIALS

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SUMMARY

The manufacture of ready made art materials flourished during the seventeenth and eighteenth centuries, whereas it did not thrive until the middle of the nineteenth century. Early records are reported. Topics discussed include changes in painting which began in the nineteenth century, i.e. factory made colors and canvas. Commercial materials and innovations are considered critically, and some of the subsequent developments in the technique of oil painting are traced.

A broad survey of literature is presented concerning the traditional manufacture of oil colors, oil purification and varnish making. Our own approach has been to demonstrate that the formulations contained in old textbooks are consistent with sound practice. Whether a manufacturer accepts this responsibility is sometimes a question.

I. Preliminary remarks: historical background

The Secreti of Don Alessio, published in Lucca 1557, contain the recipes of a "reverendo padre Gesuato pratico ed eccelente" particularly for purifying linseed oil. The ultramarine prepared by the same is mentioned by Vasari. So far as we know, the De Mayerne MS suggests the possibility that ready primed canvas was introduced some time between 1600 and 1620 (MS p. 5: "De l'Imprimeur Wallon demeurent a Londres, nomme... [sic.]") The first description of ground oil colors, to be purchased from a dealer, is made by the same MS (MS p. 84: "Huyle de lin la pinte, 5 ou 6 d. Wheit led 1 lb. broye pille en eau 5 d... Les couleurs se vendent en Pabstset allee au coing en entrant de la bourse. Les couleurs toutes broyees en la rue de Myle [sic] en allant en la guarderobbe.") The description of ready made varnishes is found in the Volpato MS.

II. Oil colors and canvas priming

The development of collapsible tin tubes as containers for colors occured during the middle years of the nineteenth century, further associated with machine-grinding, making thus the first step toward mass production: finest artist's colors, sketching and student grade colors, etc. It is of interest to note that introduction of ready made materials was accompanied by the development of Academies, whose activity centered upon aesthetic discussion and ignored the craft of painting. There is evidence to suggest a close relationship between commercial manufacture of art materials and change in preparation procedures, i.e. oil paints sold in tubes brought in certain factors which completely changed the methods of oil painting (1). Three such points are: a) ready primed canvas; b) the retouch varnish, which is a modern invention; old painters used to employ sparingly the "oiling out" technique, i.e. oil or slow drying varnish usually containing oil, for wet-in-wet painting; and c) ready made oils, varnishes, oil paints, and especially oil painting media. Unfortunately, owing to loss of studio tradition, less is known today of some of the properties of oil paints and of their use than was known to Rubens.

Regarding priming, experience gained by trial and error (the French call it tour de main) is worth more than a treatise (2). As ready primed canvas is rolled up for transport and storage, the primed surface facing inwards, it is bound always to contain less glue-size than the painter would normally apply onto it. If too oily or glossy, an oil ground may be lightly sandpapered or pumiced until it becomes matt. This gives it the tooth necessary for the adherence of the paint layers.

III. Varnish making: tradition and technological innovation

Adulterations connected with the making of art materials have always existed. When the manufacture of ready made materials became important, during the seventeenth century or so, extravagant claims have come on to the market, proclaiming themselves to be, for instance, the legendary "Venice amber varnish" (possibly a pale formulation of the old vernice liquida; Volpato mentions that both were sold in stores,) or otherwise claiming to be some kind of secret medium.

The earliest varnish and that which was most universally adopted was unquestionably the vernice liquida which consisted of sandarac or mastic (3) and linseed or walnut oil. There still is some confusion about the origin of sandarac or glassa: either from the North African Tetraclinis articulata, or juniperus resin, similar in appearance to it. We may assume that glassa, glasse aromatique, vernix, were the names given to any varnish gum, either mastic or sandarac. Next was the vernice comune which was made of linseed oil and colophony (rosin, Greek pitch, pece greca) or oleoresin. It cannot be determined whether amber was actually used, or whether the so-called amber varnish was either vernice liquida or vernice comune. We may suppose that it was customary to call amber varnish any thick and pale varnish composition. The cost was, no doubt, the chief reason why colophony or oleoresin were generally used instead of mastic or sandarac. Copal appears in the late seventeenth century (4).

Spirit varnishes were introduced about the sixteenth century. Being soluble in alcohol, sandarac was mostly used in conjunction with spirit of wine, as it must be fused before being soluble in spirit of turpentine. In fact, De Mayerne gives only one recipe calling for such a specific procedure (5).

Here are a few varnish formulations, based mainly on those manufactured over the past years by Lefranc et Bourgeois:

Final varnishes:

v. cristal	33% mastic (solvent: spirit of turpentine)	
v. Duroziez	28% mastic (solvent: spirit of turpentine)	
v. surfin	42% damar (solvent: spirit of turpentine	

v. a tableaux   44% damar (solvent: spirit of
               turpentine)

(the two damar varnishes above also contain a
small amount of slow evaporating aromatic
product; 0.5% Cosmoloid 80H microcrystalline
wax may be added to the four varnishes above
to decrease brittleness and tone down gloss)

v. mat   36% damar + beeswax (solvent:
               spirit of turpentine)
v. satine   49% damar + small amount colloidal
               silica (solvent: petroleum
               distillate)

Retouch varnishes, by volume:
v. cristal 1 part + turpentine 1 part
   (preliminary varnish)
v. cristal 1 part + turpentine 5 parts
   (retouch varnish)

Traditional final and retouch varnishes:
a) 1 oz. mastic + 2 ozs. turpentine / oil of
spike + oil

b) 1 oz. Venice Turpentine + 1 oz. turpentine
or 2 ozs. oil of spike or petroleum distillate
+ oil up to a volume equal to the rest + 1%
beeswax as suggested by De Langlais

c) 1-2 ozs. Venice Turpentine + ½ oz. mastic
+ 4 ozs. turpentine or oil of spike

Use Venice Turpentine and/or oil of spike as
slow evaporating plasticizer. When a
petroleum distillate is desired as solvent it
may be chosen according to the evaporation
rate e.g. white spirit (evaporates in one
hour) mixed with mineral spirit or kerosene
(evaporates in about twenty four hours.)
Petroleum distillate usually precipitates
resins.

Gettens and Stout (6) give a formula for
dewaxing damar in vue of obtaining a clear
solution: 80 lbs. of Batavia damar are

dissolved by agitation in a mixture of 20 lbs.
ethyl acetate and 40 lbs. petroleum distillate
(boiling range 80-180°C;) add 100 lbs.
denatured alcohol, agitate, and allow to
settle; the waxy precipitate forms a cake in
the bottom of the vessel; the clear liquid is
then decanted. Havel recommends a similar
procedure for processing damar resin. The
resin is dissolved without heat in a mixture
of 2 parts essence F (petroleum distillate)
and 1 part ethyl acetate. Three parts methanol
are added. After precipitation the liquid is
decanted. The solvent is eliminated and the
resin is washed three times with acetone
followed each time by filtration. 50% by
weight of the resin is thus obtained; it
should be soluble in white spirit, and fuse at
150°C. The well known Vibert products were
based on processed damar:

v. final (solvent: white spirit) - 44%
   processed damar
v. à retoucher (solvent: white spirit + 4%
   vaseline oil) - 20% processed damar
   containing 1/10 by weight poppy oil as
   plasticizer
v. à peindre (solvent: 1/3 white spirit +
   2/3 pétrole or kerosene) - 23% dry extract;
   equal parts processed damar and poppy oil

To clarify damar varnish made with turpentine,
a little acetone or alcohol is added in small
portions, shaking after each addition. A
white precipitate forms, which may be
redissolved by shaking. The varnish is also
clarified by repose, the precipitate settling
by itself in a few weeks.

IV. Oil vehicles; traditional methods of
manufacture and their applicability

The treatment is selected according to the
specific properties of each oil: washing,
bleaching, cold refining, degumming,
neutralization, heat processing, - are

	Linseed Oil	Walnut Oil	Poppy Oil
Raw:	coldpressed;	coldpressed;	(coldpressed;)
	washed, sunbleached;	(washed, sunbleached;)	sunbleached;
	refined + alkali;		refined + alkali;
	refined + acid;	refined + acid;	
	purified;	purified;	
	light drying;	light drying;	light drying;
	sunthickened;	sunthickened;	(sunthickened;)
	sunthickened + drier;	sunthickened + drier;	
Treated by heat:	boiled;		
	boiled + water;	boiled + water;	
	Strasburg MS formula;	Strasburg MS formula;	
	Strasburg MS formula + water;		
	(Stand Oil;)		
	boiled + water + drier;	boiled + water + drier;	(boiled + water + drier;)
	fat oil Lebrun;	fat oil Lebrun;	
	siccative oil Lebrun;	siccative oil Lebrun;	
Acid no.	1-8	2.5	1-10
Saponif. no.	190-195	190-197	190-195
Iodine no.	170-195	140-150	140-158
	naturally yellow;	medium yellow;	light yellow;
	dries very fast;	dries fast;	slow drying;
	medium acidity;	the least acid;	most acid;
	saponifies like poppy oil;	difficult to saponify;	saponifies like linseed oil;
	yellows most;	yellows slightly;	yellows slightly;
	by heat processing becomes pale but more viscous and yellows less, however is more easily saponified;	does not need heat treatment but gives fluid or non yellowing product by heating with drier;	does not need heat treatment.

TABLE I

```
washed/sunbleached + water                    ──────────── sunthickened;
   (Gesuato, Nunez;)

purified: ┌ breadcrumbs;              ┐
          │ salt;                     │
          │ sand;                     ├ + water
          │ alum;                     │
          └ yolk/spirit of wine       ┘

          alkali    ┌ ¼ lime (linseed oil;)
          refined:  └ Venice glass (poppy oil;)

Cold-      filtered   acid     ┌ urine (walnut oil;)
pressed;   (charcoal, refined:  ┤ vinegar + alum (linseed oil,
           sand;)              └    Italian recipe;)

          light     ┌ lead white;
          drying:   │ lead white + lime;
                    │ lead white + other             ──────── sunthickened
                    │   ingredients;                          drying.
                    │ vinegar + litharge
                    │   (linseed oil;)
                    │ lead white/litharge/zinc
                    └   sulphate + water (poppy oil;)

          boiled:   ┌ alone (linseed oil;)
                    │ + water (walnut oil;)
                    │ Strasburg MS recipe (linseed,
                    │   walnut oil;)
                    │ Strasburg MS recipe + water
                    │   (linseed oil, Dutch recipe;)
                    ├─────────────────
                    │ drier + water (linseed/walnut oil;)
                    │ fat oil (linseed/walnut oil;)
                    └ siccative oil (linseed/walnut oil;)
```
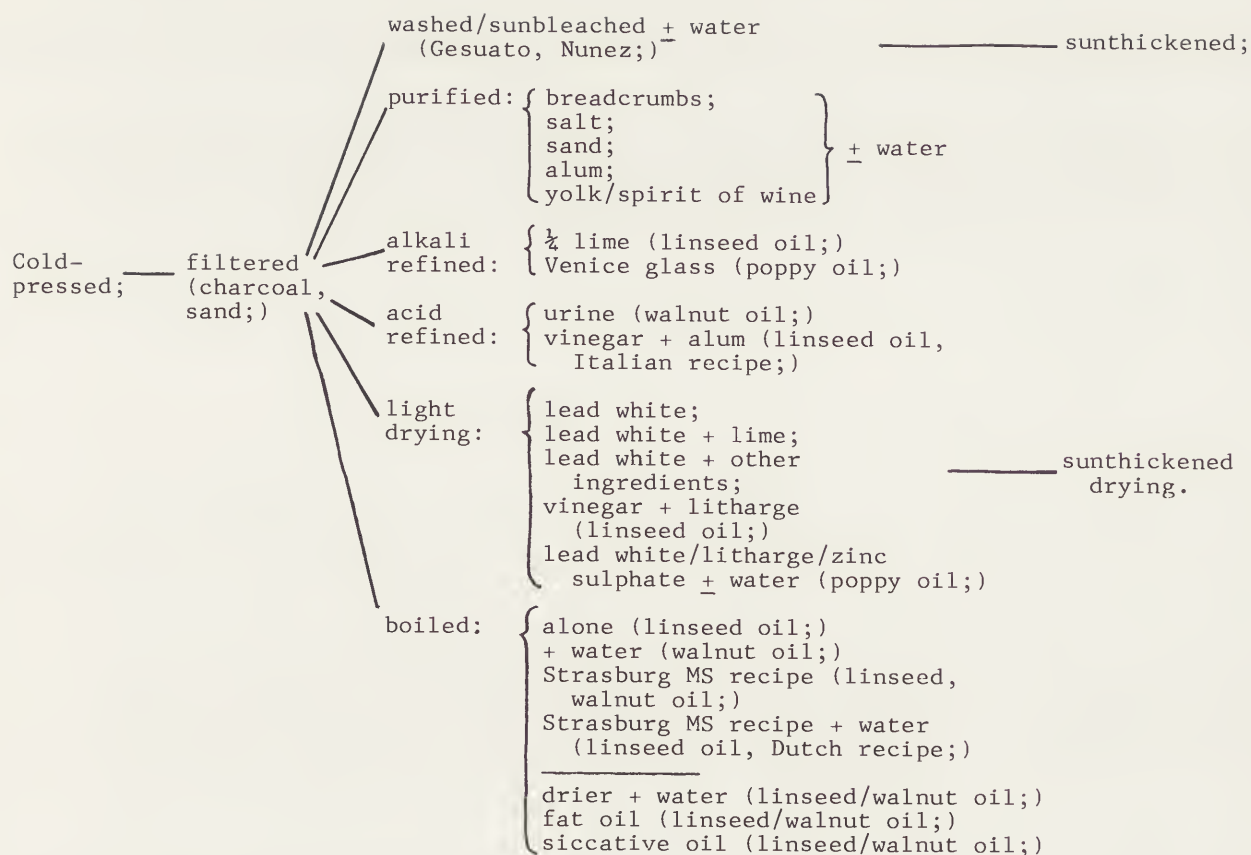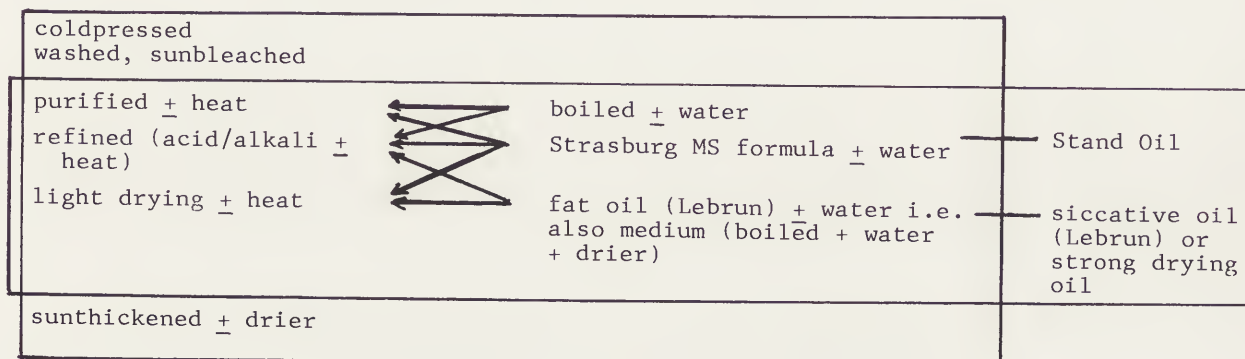
TABLE II

selected and combined with a thorough knowledge of the raw materials and final product desired. This knowledge may be one of the causes of the excellent conservation of old Masters' paintings (7). Heat reduces iodine no.; oils with low oidine no. yellow less. Pale boiled oils can be obtained by regulation of the heat treatment. Another method is to dissolve the maximum quantity of metallic oxides in a small portion of the oil and then add this to the bulk of the raw oil, which is heated to just sufficient temperature to cause the break to coagulate and separate out, e.g. Lebrun's fat oil (8). The various methods may be proposed in a practical sequence (9): a) prefiltration (charcoal) in vue of clarification, or: b) serial filtration (accomplished as the oil passes through progressively smaller pore size filters, e.g. sand, linen cloth, felt;) c) cold refining by contact (adsorbtive substances, acids, alkali) e.g. purification and/or neutralization; d) decolorizing (bleaching) by the above processes and by exposure to sun;

RAW OIL (Cennini, Le Begue)

```
┌──────────────────────────────────────────────────────────────────────┐
│ coldpressed                                                            │
│ washed, sunbleached                                                    │
│ ┌──────────────────────────────────────────────────────────┐          │
│ │ purified + heat        ↙↖  boiled + water                 │          │
│ │ refined (acid/alkali +  ⤫  Strasburg MS formula + water ──┼── Stand Oil
│ │    heat)                ⤫                                 │          │
│ │ light drying + heat    ↙↖  fat oil (Lebrun) + water i.e. ─┼── siccative oil
│ │                            also medium (boiled + water   │    (Lebrun) or
│ │                            + drier)                      │    strong drying
│ │                                                          │    oil
│ └──────────────────────────────────────────────────────────┘          │
│ sunthickened + drier                                                   │
└──────────────────────────────────────────────────────────────────────┘
```

BOILED OIL
(Strasburg MS, Eraclius)

TABLE III

e) heat processing. Purification and
refining methods accelerate the process and
build in certain properties; the product is
more fit for grinding and therefore is not
useful for further sunthickening. However,
such methods are not necessary as washing and
sunbleaching will give, in due time, a fine
grinding oil. On the other hand, sunbleached
or even coldpressed and filtered walnut or
poppy oil are so light that they do not need
further processing (10).

During winter, or when weather is particularly
damp, oil colors dry more slowly. Nicolae
Tonitza, a Romanian painter, recommends to
mix in with every color on the palette a drop
of boiled linseed oil prepared without driers,
for the right consistency. This is done with
a palette knife. During summer, a drop of
raw linseed oil is quite sufficient.

These general facts about oil painting
materials will enable us to follow any account
of the old recipes (11). Morandi would spend
long hours preparing his own canvas, and
grinding his own colors. In fact, if a
paint is worth making, it is worth making
well. In recent decades, new materials have
come into use for modern painting. Synthetic
resins have taken the place of the old gums,
resins, and glues. The artist rarely knows
precisely the type of ingredients and almost
never is aware of their behaviour.
Unfortunately, materials brought into use
often are badly adapted to survival of the
work.

Footnotes and references

1 V. and R. Borradaile, eds. and trans.,
   The Strasburg Manuscript, a Medieval
   Painter's Handbook (London: Tiranti, 1966)
   p. 54: "The colors must be ground in the
   oil and also tempered with the oil, all
   colors being ground thick and then tempered
   to the consistency of a soft paste, neither
   too thick nor too thin... grind in three
   drops of varnish to every color... to all
   colors add a little white calcined bone
   dust or a little zinc vitriol, as much as
   a bean, in order to make them dry."
   For the nature of the oil and varnish above
   see S.C.Arteni, "The Strasburg Manuscript,
   a Compendium of Van Eyck's Materials and
   Techniques," Proc. I.S.F. 14, 1978
   (Correggio: SIRAI, 1980), p. 127-134.
   Marciana MS sixteenth century in
   M.P.Merrifield, trans., Original Treatises
   on the Arts of Painting (New York: Dover,
   1967), p. 626: "Grind the color with
   linseed or walnut oil as stiff as you can
   i.e. with as little oil as possible and so
   that it may be very fine; on being felt
   between the fingers no hard grains should
   be perceived; when you paint, if it is
   too stiff, dip the brush in a little oil
   and incorporate it well with the paste."
   Volpato MS about 1700 in Merrifield, op.
   cit., p. 739: "S. Come si neta le petre
   quando si è macinato li colori ? F. Con
   la semola di formento e poi con un pezzo di
   stratio, e cosi istessamente le tavolozze;
   ma averti che quando la semola non e piu
   stata adoperata, lascia qualche poco di
   farina si che habi l'actio, che se
   macinarai laca fina o verde eterno
   bianchegiono e si guastono, e percio la
   semola e meglio come si è adoperata diverse
   volte. S. E se per caso si scordasse di
   netar che il color si secasse, come si
   neta? F. Con un poca d'acqua et una pietra
   pomice."
   U.Forni, Manuale del Pittore Restauratore
   (Firenze: Le Monnier, 1866), p. 145:
   "Ogni colore si macina sulla pietra o sul

cristallo con olio di papavero, di noce o
di lino già purificati, procurando far di
ciascuno una pasta che non coli, cioè
molto soda. Quanto piu si macinano, tanto
meglio rispondono all'uso... Fatto questo,
si mettono in tubi di piombo, verniciati
di dentro con vernice a spirito [i.e.
alcohol.]"
From the mid nineteenth century on,
machine grinding will gradually replace the
hand-grinding methods cited here.

2 Volpato MS in Merrifield, op. cit.,
   p. 729-733: "... sarai havertito che le
   telle sijono buone, forte, liscie, ben
   lavorate, che con poca materia restino
   impresse...; le telle liscie poca materia
   l'imprime; che come vi è troppa materia
   anerisse li colori per l'abondanza de
   l'olio che vi si pone ed il replicar molte
   primiture; e pero piglia buona tela, e
   tirata in telaro, gli darai una mano di
   colla di retagli di nonnate o maschiette
   per che riesce piu dolce, che le colle
   come di bergamina, essendo forte e crude,
   fa certe ritiramente nelle telle che fa
   cativo efetto... asciuta la lisciarai con
   la pomice, e li darai un altra mano di
   cola come prima et osserverai, che non si
   troppo dolce ne troppo forte, la troppo
   dolce non difende la tela dall'olio, e la
   troppo forte fa crepar il colore, e la
   buona serà tenera come gelo quando è
   rafredata... S. Per conoscere la cola
   quando si fà, se è troppo forte, o
   dolce, perchè si da calda? F. Io toco
   con due dita e sento se ha picico nel
   asciugarsi, e da quelo m'accorgo, se è
   troppo forte v'agiungo dell' acqua e lascio
   levar il bolo, e se è dolce la lascio
   bolir fino che mi pare fatta giusto al
   bisogno... io adopro cola semplice come ti
   ho detto, che data doi volte apomicando
   ogni volta dopo asciuta acio la tela venga
   liscia, li do poi la primitura macinata ad
   olio di lino, e tutte le terre sono buone
   per questa faccenda... le do con il cortelo
   supra dela tela, e dopo asciuta e pomicata,
   le do un altra mano macinata... la seconda
   mano poco colore fa bisogno... Con il
   gesso si gioca di fortuna... il che
   proviene dalla qualita della cola... la
   meglio è la dolce... et in questo modo, ci
   vol pochissimo gesso... che quelle che
   hanno poco gesso si conservano... e cio si
   conosce dala tessitura dela tela che si
   scopre li relevi di detta, ben chè habia
   gesso, primitura, e colori...."
   Gesso for canvas adapted from L.Lamb,
   Materials and Methods of Painting (London:
   Oxford University Press, 1970), p. 62:
   take equal measures of chalk, lead white
   and liquid glue; mix the powders on a slab
   with the palette knife and work in the
   glue; brush thinly onto the canvas.
   Gesso ground for panels, Ibid., p. 67:
   fill 1/3 of a glass container with warm
   glue and drop in the powdered chalk but do
   not stir; as soon as the rising level of
   the chalk has reached the top of the glue,
   put the glass in the upper part of a double
   boiler and heat; it can now be stirred.

3 See Strasburg Manuscript, op. cit.

4 Copal is mentioned by Palomino. Copal
   varnish is prepared as follows: a) gum
   running (by heating until it is in a quiet
   state of ebullition and there is no more
   frothing;) b) oil boiling at 500°F for
   1 to 2 hours; c) mixing (the oil is
   poured into the melted gum stirring all the
   time;) d) boiling the mixture (at
   450-500°F for ½ hour up to 4 or 5 hours
   until the liquid has stringiness;)
   e) thinning (turpentine is added in small

quantities at a time stirring well;)
f) clearing and ageing for six months to
two years.
See De Mayerne in E.Berger, ed. and trans.
Beitrage zur Entwickelungsgeschichte der
Maltechnik (Munich: Callwey, 1901-1912),
IV, p. 178 for amber (carabé) varnish
(for the preparation of the oil according
to De Mayerne see footnote 7; the oil is
boiled before being mixed with the resin:)
"M. de la Garde. NB. Venu d'un excellent
faisseur de Luths... Le feu soit petit au
commencement puis bien fort;... quelques
fois il fault deux heures, ou plus devant
qu'il fonde en liqueur; remués souvent...
Rp. Carabé le plus jaune tirant sur le
rougeastre tant que vous voudrés. Mettés
le dans un pot de terre plombé sans y
adjouster aulcune chose. Laissés le sur un
feu mediocre, ardent de charbon, le
remuant avec un morceau de fer. Il se fond
en un corps obscur qui semble de la
Colophone. Estant fondu versés de dessus
du papier ou sur une pierre de marbre...
Rp. de... huile une pinte de Londres, ou
chopine de Paris, Carabé preparé comme
dessus, pile subtilement, six onces
environ, mettés à chauffer à petit feu
avec vostre huile... en remuant tousjours...
Ainsy vostre vernix est faict, qui se
guardera tant plus tant mieux."

5 See S.C.Arteni, "Inquiry into the Nature
   of Oils and Varnishes used in the Low
   Countries," Proc. I.S.F. 14, op. cit.,
   p. 113-124, footnote 51, for sandarac
   varnish with turpentine spirit.
   See also De Mayerne in Berger, p. 108:
   "Couleurs se peuvent toutes vernir. Bon
   vernix. Rp. huyle blanc de Therebentine
   deux onces. Therebentine tres belle et
   fort blanche une once. Sandarach tres peu.
   Fondés doulcement la Therebentine seule,
   estant fondue dans eau chaude, adjoustés
   y l'huile et quand tout sera bien meslé
   ostés de l'eau chaude. La Sandaracha soit
   fondue a part avec un peu dudicte huyle,
   puis l'adjoustés a tout le reste meslé,
   estant chaud. L'huyle en attirera ce qu'il
   pourra. (n... mettés vos matieres dans un
   pot de terre couvert, sur sable chaud...
   Belcam.)

6 R.J. Gettens and G.L.Stout, Painting
   Materials, a Short Encyclopaedia (New York:
   Dover, 1966), p. 17.
   An extraction-precipitation process is
   mentioned by De Mayerne in Berger, p. 350:
   "Vernix d'ambre. - Il fault avec du trespur
   esprit de vin, extraire la teincture, ou
   partie sulphurée dissoluble, de l'Ambre...
   par plusieurs infusions au sable.
   Precipités dans de l'eau... Laissés rasseoir
   par quelques jours. Versés vostre liqueur
   claire par inclination, ou bien la separés
   d'avec l'ambre par les languettes de
   feultre, et laissés seicher la poudre qui
   restera, sur du papier blanc qui boive,
   ou bien sur de la Croye, et la guardés en
   lieu sec... Cette extraction de resine se
   faict hors du Benjoin, Storax, possible
   aussi du Mastich et du Sandarach, ou
   gomme de Geneure. Voyés de la Gomme Lacque
   (fit.)...."

7. See J.Blockx 1922; Nunez 1615; and
   especially "Secreti aggiunti... havuti da
   un reverendo Padre Jesuato" in Secreti di
   Don Alessio (Lucca: 1557): "Piglia oglio
   fatto di semelino bello e chiaro del color
   croceo cio è color d'oro e quella quantità
   che a te pare e mettile in un corno di
   vetro over di bue, e che habbia un
   buchetto in fondo, e metteci sopra acqua
   fresca, e con un legnetto lavalo bene
   mesticandolo sottosopra; poi lassalo

alquanto posare et apri il buco di sotto
e lassa andar via l'acqua, e a questo
modo farvi per sette o otto volte, overo
tante volte che l'acqua venghi fuora
chiara si come tu ce la metti, et a questo
modo si purifica il detto oglio; poi
conservalo in ampolla di vetro alli tuoi
bisogni...."
See De Mayerne in Berger, p. 134 for a
filtration method: "Huyle de noix ou de
Lin passée par une chausse d'hypocras sur
de la cendre de serment devient claire."
Varnish oil is prepared by two methods
according to De Mayerne in Berger,
p. 178-180 (compare with linseed oil for
mordants, purified, according to the
Marciana MS, by boiling the oil with
water:) "Pour desgraisser l'huile prenés
de l'huile de Lin toute pure, mettées la
dans un pot plombé neuf sur le feu,
laissés bien bouillir, ayant bouilly et
l'ayant bien escumée, prenés une plume
d'oye ou de poule, et la trempés dedans,
si la plume brusle, l'huile n'est pas
assés desgraissée, continues a bouillir
jusques à tant qu'elle ne brusle point la
plume. Passés par un linge... L'huile de
lin se desgraisse en la battant dans une
bouteille de verre avec moitié eau fort
long temps, laissés le 15 jours ou trois
septmaines, il se faict comme graisse
blanche entre l'eau et l'huile qui se
separera par inclination de cette graisse."

8 See Fra Fortunato (1659-1711):
   "Per far l'olio cotto da pittore, che sia
   chiaro come acqua.- Metti il solito
   piumazzolo col litargirio et altro come
   si usa dentro l'oglio di noce o di lino a
   bollire, e con esso mettivi seco dell'
   acqua a bollire, che questa lo fara
   rimaner chiara, come l'acqua medesima."
   See also Lebrun 1635 in Merrifield, p. 817:
   "L'huile siccative se fait mettant en une
   chopine de l'huile de noix dans laquelle on
   y met un linge plain de terre d'ombre et
   de mine, que l'on pend à lance du pot,
   puis la fait on bouillir. Huile grasse se
   fait avec de la litarge que l'on met dans
   un sachet en une chopine avec de l'huile,
   puis on la fait bouillir. Autrement on
   broie la litarge avec huile sur le porphyre,
   et en fait on petite balle que l'on fait
   seicher, puis quand on s'en veult servir,
   on les fait bouillir jusques a ce que la
   litarge soit fondue; puis estant froide,
   elle devient claire comme eau de roche."

9 See S.C.Arteni, "Notes on Artists'
   Materials," Proc. I.S.F. 14, op. cit.,
   for a discussion of oils and varnishes.

10 See G.Secco Suardo, Il Restauratore dei
   Dipinti (milano: Hoepli, 1927), p. 499
   for light drying linseed oil: "Il prof.
   Guizzardi di Bologna... poneva in una fiala
   quattro parti di olio di lino spresso a
   freddo ed una parte di litargirio ben
   macinato. Esponeva quella fiala al sole e
   ve la lasciava tutta intiera una state,
   scuotendola di frequente. Alla fine
   decantava quell'olio, vi aggiungeva del
   carbone polverizzato, e dopo aver agitato
   il miscuglio e lasciatolo per alcune ore in
   riposo, lo filtrava attraverso della carta,
   ottenendo in tal modo un olio limpido,
   scorrevole ed essicatissimo. Poneva sulla
   tavolozza i colori macinati ad olio nel
   modo consueto, e prima di valersene
   intingeva il penello in quell'olio."

11 Materials mentioned above as well as in our
   former papers were available in the trade
   up to 1977. Since then some have either
   dissapeared, e.g. Winsor & Newton's water
   color cakes, or have changed composition,

e.g. Vibert products now made of synthetic
resin. Some oil color brands have changed
the composition of vehicles, e.g. Old
Holland introduced since 1978 poppy oil
for grinding. See De Mayerne in Berger,
p. 120 for brushes: "Pinceaulx. Fault
avoir des broisses de poil de pourceau le
plus doulx. Courtes et espaisses sont les
meilleures pour esbaucher un tableau.
Apres en avoir peint, de peur qu'elles ne
se seichent soyent misent dans l'eau, si
elles sont seiches soyent frottées de
savon, lavées et rincées avec eau chaude.
Pour les arbres et pour esbaucher ce qui
est le plus menu fault avoir des pinceaux
de poisson [sable?] longuets et firmes.
Pour le reste des pinceaulx de queue
de gris gros et courts, pour faire les
troncs des arbres, et tirer des longues
lignes... Apres avoir peint nettoyés bien
vos pinceaulx, et les tenés en l'huile
de peur qu'ils ne se seichent."

Appendix

Spirit of wine came into use for the
preparation of varnish in the sixteenth
century; in a suitably diluted form, the
recipes below may be useful for the
formulation of varnishes.

Benzoin (it is quite soft at 75°C and fluid at
100°C; alcohol dissolves most of it:)
Marciana MS in Merrifield, p. 629-631
("Item vernice ottima la quale si fa senza
fuoco, et seccha senza sole prestissimo, et
resta molto chiara, et si puo vernicare ogni
lavoro dipinto in tavola o in cartoni o sul
ferro. Togli acqua vite che sia passata tre
volte almanco... et togli del bengivi et
mettivene dentro quella quantita, tutta a un
tratto o a poco a poco che sia abastanza...
diguaza tanto che il bengivi si solva... ti
resta come vernice liquida buona....")
De Mayerne in Berger, p. 184 ("Vernix de
Benjoin sur or. Versés sur du Benjoin
trespur subtilement pulverisé, du bon esprit
de vin, qui surnage de deux doigts. Laissés
le deux ou trois jours, y adjoustant
quelques poils de saffran. Le Benjoin se
fondra en partie dans l'esprit de vin.")

Sandarac and oleoresin (sandarac is valued on
account of the hardness and lustre of the coat
it forms; it melts at about 150°C:)
Paduan MS in Merrifield, p. 691 ("Vernice
lucidissima per pitture e carte alla fiamenga.
R. oz. 7 acquevita sflemattma oz. due
Sandaraca, oz. due abiezzo. La sandaraca
sia ben chiara si polverizzi, e si meti in
bozza insieme con l'abiezzo, che deve essere
chiarissimo, et poi ponivi l'acquevite, e
falla bollire dolcemte al foco sino che tutto
diventi acqua tenendo stopata la bozza accio
l'acqua vite non svapori, e poi si coli in
vaso di vetro facendo restar a dietro il
fondo....")
Ibid., p. 697 ("La vernice si fa come sotto.
Oz. una gomma di ginepro, oz. ¼ oglio
d'abezzo puro e chiaro... oz. ½ acqua vite
bonissma di sette cotte. Si macina la
sandaracca e si fa pasta con l'abiezzo e si
mette in bozza, e se li mette sopra la dta
acquavite e si mette sopra fuoco dolce, tanto
che il tutto s'incorpori, fatto questo con
pennello di piuma si pinge il legno, o vetro
se vole invernigare.")
De Mayerne in Berger, p. 292 ("Eau de vie
qui brusle toute puis faut prendre 1 oz. de
sandarac du plus blanc et clair mis en poudre
fine, et le gros d'une amande de therebentine
de venise et mettre premierement la poudre et
la therebentine dedans la fiole et puis l'eau
de vie. Et mettre la fiole sur le feu doux

a petit feu jusques ace que le tout soit
fondu et pour le faire plus beau on le peut
sy on veut passer par un linge.")

Sandarac, oleoresin and mastic
Paduan MS in Merrifield, p. 697 ("Vernice
chiara. Lib. una spirito di vino, oz. 4
trementina fina, un quarto d'oncia di
mastice bianco, et un quarto di sandracca,
il tutto messo in boccia... e le si da fuoco
per sei hore pero di sabia tantoche si vede
a bollire, e poi e fatta.")

NOTE ON THE PAINTING TECHNIQUE OF Melchior
                           BROEDERLAM

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_____

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ABSTRACT

Two painted wings of the Crucifixion altar-
piece by M. Broederlam ,dated 1396 and belong-
ing to the museum of Fine Arts of Dijon,have
been examined microscopically,and paint sam-
ples have been analysed by microchemistry and
microprobe. Knowing the stratigraphy and the
composition of the different paint layers,the
painting technique of Broederlam could be re-
constructed and compared to other schools and
painters,with special reference to Van Eyck.

The mean difference between both masters was
found to rest in their binding medium; an
emulsion in each case,but the one of Broeder-
lam being close to a protein tempera whereas
that of Van Eyck is almost an oil paint.

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                o   o

The technique of M. Broederlam, precursor of
Van Eyck and considered as the first Flemish
Primitive,has been studied by scientific exa-
mination on the wings of the Crucifixion altar
piece belonging to the museum of Dijon. These
wings,dated 1396, are the sole easel paintings
attributable with certainty to this master.

Though the sculptures on the inside of these
wings have probably been polychromed by the
painter himself,we do not consider them here,
but their study will be published elsewhere.(1)
Samples taken on existing damages have been
examined by microchemistry,completed with
microscopical observations on the paintings
and assisted in some cases by microprobe ana-
lysis. *

The panels seem to be of oak,as could be obser-
ved on the frame,with which they make an entity,
but no analysis of the wood could be done.
The panels are lined with a flax canvas (**),
presumably covering the whole area and over-
running the frame. Both parts are gilded with-
out discontinuity and show the same punched

decoration. The whitish ground,nearly one
millimeter thick,is composed of chalk with
coccoliths and very little glue,making it look
quite porous. This ground is slightly impreg-
nated with animal glue near the surface,pro-
bably due to an isolating layer.

Left wing: Annunciation an Visitation

The underdrawing shines through the veil of
saint Elisabeth,the lectern and the rocks. A
gap in the right index of the Virgin shows the
drawing to be made of a dark brown line on the
white ground. A cross-section through the flesh
tone shows a thin layer (5 to 10 μ) of red
earth and charcoal,situated between the ground
and a white ground tone. As this brown colour
corresponds to that of the line visible in the
gap,we may admit that it is the drawing.
Lines engraved in the ground trace the outlines
of the gilding,and the larger painted areas
are reserved in the gilding. Under the gold
foil the ground is covered with a thin layer
(5 to 10 μ) of red bole with tempera,probably
animal glue. After this gilding the painted
parts have been given a ground layer of lead
white and mixed protein-oil medium;its thick-
ness ranging from 10 to 30 μ.

The different colours sampled and examined re-
veal the following structure and composition:

Blues: Mantle of the Virgin and angels:

On the dried ground layer of lead white have
been painted successively a light blue of coar-
se ultramarine and white lead with protein-
based binder (10 to 25 μ),followed by pure
coarse ultramarine with protein tempera,probab-
ly in two parts strongy linked together and of
total thickness between 40 and 100 μ.

Green: gown of saint Elisabeth:

This colour appears as a thick opaque layer
(25 to 50 μ) of copper green and lead white,
with a medium on base of proteins. At least
four greyish layers without grains separate
this part from a greenish grey,that should
thus be considered as an overpaint.

Green; foliage:

On the white ground tone has been applied a
light green,similar to that of the gown (10 to
20 μ),followed by a green glaze,probably of
copper resinate (10 to 20 μ). In the lighter
parts a third layer,again a mixture of white
and coppergreen has been found on top of the

glaze.

Ocre yellow of a door:

The yellow on the white underpaint only contains lead,probably massicot,and a yellow dye mixed with very few grains of cinnabar (20 μ) and an emulsion like medium. The thin brown layer without grains (5 μ),seems to be an original oily or resinous glaze.

Bright yellow from an angel:

The white ground layer contains traces of ultramarine in the upper part. A layer of lead-tin yellow II (15 μ) with protein-oil emulsion has been applied on the dried ground layer.(2) The beige layer (5 μ),which covers the yellow, probably is not an original glaze.

Bright red,gown of saint Elisabeth:

On the white groundtone; vermilion (cinnabar) and a mixed medium on protein base,which seems to be painted in two times.(20 to 30 μ)

Dark red on gilded brocade:

The gold foil,probably on red bole,is missing on the cross section. Vermilion with protein-based medium (5 to 40 μ) is covered by a thick dark red oily glaze (75 μ).

Light flesh colour of a hand:

On the white ground tone lays a very light greenish grey,followed by a thick layer (30 to 50 μ) of white lead,a little vermilion and a few grains of organic red. The medium being a mixture of oil and proteins.

Flesh tone (shadow),of the same hand:

Here too a green underpaint of leadwhite,copper green and traces of charcoal,with mixed medium is present. The upper layer being a kind of glaze (5 to 10 μ) containing very little red earth and charcoal. The black pigment does contain no phosporus and thus is probably of vegetal origin.

Dark brown from the rocks:

The whitish groundlayer contains a few black grains and is covered with a transparent brown containg a little red earth and charcoal (10 to 15 μ) and oil-based medium. The oily layer with traces of red (10 μ) is probably an overpaint.

Light grey of a phylactery:

On the white ground tone a mixture of white lead,ultramarine and probably a little red lake (10 μ) has been painted with a mixed binding medium.

Gilding of the background and the frame:

The red bole,probably with animal glue (5 to 10 μ) covers the chalk ground. A gold foil, less than 5 μ thick has probably been fixed to it with no other adhesive but the wetted binder of the seat. The gold foil has been burnished bright and puched afterwards.

Right wing :Presentation at the Temple and
———————— Flight to Egypt:

The chalk ground and white ground layer are similar to those on the left panel.

Violet,mantle of Saint Simeon:

The white ground layer has been covered by a mixture of lead white,ultramarine and organic red; the medium being of the mixed type,on base of proteins (15 to 30 μ).

Dark green of foliage:

Similar to the corresponding colour on the left wing.

Brownish green of the soil:

Still on a white ground layer lays a greyish copper green,with mixed medium (5 μ),under a layer of copper green with some grains of charcoal and white (30 to 40 μ).

Bright red,clothes of Saint Joseph:

Same structure and composition as the dress of Saint Elisabeth on the left wing.

Witish;temple,tower and column:

A layer of white lead with traces of black has been painted on the white ground,probably while still fresh. The media of both parts reacting as a protein-oil mixture. In one of the three samples a trace of black (5 μ) is present between the chalk ground and the lead white,possibly a part of the drawing.

CONCLUSION :

The elaboration of these painted wings can be
conceived as follows: Directly on the chalk
ground the painter has situated the outlines
of the coloured elements,with a brownish tem-
pera laid on with a brush. In some parts
hatched shading lines are intended to be co-
vered with a dark glaze and take part in the
final colour. Then the outlines of the gold
foil are engraved in the ground and filled
with red bole. After the gold has been polis-
hed,a white groundlayer is painted on the
parts to be coloured,except under the trans-
parent browns,where the imprimatura seems to
be greyish.

Next come the different colours: violet is
obtained by mixing ultramarine and a red lake.
Blues are composed of a light blue undertone
followed by pure ultramarine with tempera,
probably applied in two layers. Greens also
are composed of two parts; first a mixture of
white and green,and then a glaze of rather
pure green that may contain a few grains of
charcoal. The green pigment contains copper,
but its exact nature could not be identified;
maybe it is an opaque resinate treated as a
grainy pigment. In the transparent layers it
could be mixed with oil or resin to form a
glaze similar to the "molten" kind of copper
resinate.(3),(4).

The bright yellow is painted in one layer of
pure lead-tin yellow,whereas the darker one
seems to be a mixture of massicot with a yel-
low dye and very few grains of cinnabar (20 µ)
the whole being probably glazed with an orga-
nic yellow.

The bright reds too are laid on in one layer,
pure vermilion,probably cinnabar,whereas dark
reds bear a thick oily glaze of a non identi-
fied lake.

The transparent browns of the rocks are obtai-
ned by laying a kind of oily glaze with a few
pigment grains on the ground layer,modelled by
the dark brown drawing.

Light flesh tones are made by superimposing a
thick pink layer on a light green ground tone;
whereas in the shades, the green underpaint
becomes darker and the upper layer brownish
and very thin,making the green shining through
more strongly.

Whitish greys are brushed in one layer of lead
white with some blue and red grains,but with-
out black pigment.

The binding medium generally is a kind of
emulsion near to protein tempera,containing a
little oil,excepted in the brown and red gla-
zes that are oily. The ultramarine,on the
other hand reacts as a pure protein tempera.

These results show that the stylistic affinity
of Broederlam with the Italian Primitives of
the trecento is also reflected materially; for
instance by the use of lead-tin yellow contai-
ning silica,of ultramarine as only blue,and of
a binding medium close to egg tempera. Also
through the use of a green imprimatura under
the flesh tones,as well as the abundance of
gilded backgrounds.

On the other hand do the oaken panels and the
chalk ground reveal the northern origin of the
artist. The construction by successive co-
loured layers of increasing saturation,as well
as the modulation of their relative thicknes-
ses and the search for shading by varying the
medium,do announce the Flemish Primitives.

Others did compare the technique of Broederlam
to that of the Czechs Primitives,but there too,
the correspondence is only partial.

Comparison with Van Eyck brings out several
common features,such as the stratigraphy of
successive covering layers with a final glaze,
like in the greens and dark reds. Also the
pigments used by both,even if Van Eyck's palet-
te richer.

The differences,however,are more important;for
instance the overall aspect of the colours,
more opaque and colder on Broederlam's pain-
tings,where no blue glazes are found,and where
the general modelling is rather weak.
His green glazes,on the other hand,seem less
transparent than Van Eyck's ones,and do not
show the brownish "tempering" in the foliages
etc. Van Eyck's flesh tones are very often
laid on a light greyish imprimatura instead of
a green one,and his brocades are full painted
but not constructed on real gold as Broederlam
would do.

The most profound difference rests in the bin-
ding medium; both painters use a kind of emul-
sion,but that of Broederlam is close to egg
tempera whereas the one of Van Eyck is based
on oil. This inversion of the emulsion appears
to be the real innovation of Van Eyck and is
more positive for the saturation of his enamel
like colours than the structure by successive
thin layers.

Conclusively we may state that both masters   ples.
have so different techniques that the one can-
not be considered as the continuer of the
other.

Though he belongs to the international style,
with a technique close to that of the Italian
Primitives,Broederlam cannot be classified
satisfactorily in any school,since he has for-
ged the adopted foreign elements into a perso-
nal way of painting. Anyhow he has formed a
bridge between the Italian Primitives and Van
Eyck.

Notes:
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* Analysis with the microprobe was done at the
I.R.P.A. by Mr L. Maes.

** Microchemical identification by Mr Vynckier

          B I B L I O G R A P H Y
          ————————————————

1. COMBLEN M. " Corpus du Musée des Beaux-Arts
              de Dijon "
              Centre des Primitifs flamands -
              Bruxelles (to be published in
              1984).

2. KUHN H. " Lead-Tin Yellow "
              Studies in Conservation 13 (1968)
              Nr 1 p. 7.

3. KUHN H. " Verdigris and Copper Resinate "
              Studies in Conservation 15 (1970)
              Nr 1 p.12.

4. KOCKAERT L. " Note on the Green and Brown
              Glazes of old Paintings "
              Studies in Conservation 24 (1979)
              Nr 2 p.69.

PIGMENTS IN CHINA - A PRELIMINARY BIBLIOGRAPHY OF IDENTIFICATIONS

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Summary

In contrast to the situation for Japanese materials, there have been few identifications reported of Chinese painting pigments. This report lists those known to the author, with annotations and introductory comments.

Introduction

This report lists those publications known to me of the identifications of pigments or pigment materials in paintings, or in other historical or archaeological sources, from China. There is no attempt to deal with purely historical evidence on this subject, for which such writings as those of Needham (1) may be consulted.

It will be seen that the publications are few, scattered, and relate to no systematic body of work. This situation contrasts with that for Japanese pigment studies, where we may point to the investigations of Yamasaki and co-workers (2), as well as of others (3). Indeed, it seems fair to say that East Asian pigment history is dominated by work on Japanese materials at the present time. It would be pointless to discuss in detail specific reasons for this state of affairs, which may be related as much to the existence in Chinese art history of important schools of painting having little use for highly coloured palettes as to the lack in that country of workers having pigment history as their foremost area of interest.

There are one or two points that do require comment, however. First, this list is probably incomplete, particularly as regards publications from People's Republic of China. This is a difficult area of the literature to cover, not only because of the language barrier but also because many relevant publications may enjoy only a limited circulation within that country. Certainly, I should be most grateful for additions and emendations.

Secondly, meagre as it may be, this listing does contain a tantalizing historical point. Two of the papers give clear identifications, from very early sources, of substances not usually found as pigments elsewhere: thus, Entry 5 describes a barium analogue of Egyptian Blue in several artifacts from the Han dynasty or earlier, and Entry 13 describes lead sulphide and sericite, as well as the black, cubic form of mercuric sulphide (which may perhaps be an alteration product) on a painted textile from the Han dynasty. If more early materials should become available, Chinese pigment history may turn out to be more interesting than we suspected.

The bibliography does not include investigations of materials that have long been kept in some other country, but that may well have had a Chinese origin. Those in the Shōsōin repository in Nara, Japan, are the obvious case, and they have attracted study (4). On the other hand, certain publications are included (Entries 2, 11) that describe known pigments actually appearing in collections of "minerals" or "medicinals" and the like. With this, the bibliography of pigment identifications in China is presented.

Notes to Introduction

(1) Needham, J. and co-workers, Science and Civilisation in China, Cambridge University Press, from 1954. See especially Vol. 5 Part 2 (1974), and Vol. 5 Part 3 (1976).

(2) Best recent summary: Yamasaki, K., Emoto, Y., 'Pigments used on Japanese paintings from the protohistoric period through the 17th century,' Ars Orientalis, 1979, Vol. 11, 1-14.

(3) E.g.: FitzHugh, E.W., 'A pigment census of ukiyo-e paintings in the Freer Gallery of Art,' Ars Orientalis, 1979, Vol. 11, 27-38; Taguchi, E., Taguchi, M., 'Spectrophotometric identifications of color materials, especially of organic pigments and their mixtures, with reference to the pigments used in the scroll "Genji monogatari 54-jo emaki" of the Edo period,' Kobunkazai no Kagaku, 1977, Nos. 20-21, 18-37.

(4) Asahina, T., Shōsōin Yakubutsu, Osaka 1955; Masutomi, K., Shōsōin Yakubutsu o Chūshin to suru Kodai Sekiyaku no Kenkyū, Kyōto 1957.

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1. Benedetti-Pichler, A.A., 'Microchemical analysis of pigments used in the fossae of the incisions of Chinese oracle bones,' Industrial and Engineering Chemistry, Analytical Edition, 1937, Vol. 9(3), 149-152.

The oracle bones were of the Shang dynasty, from An-yang. Red mercuric sulphide was identified microchemically, and a black pigment was found to be "carbonaceous". See also: Britton, R.S., Benedetti-Pichler, A.A., 'Oracle-bone color pigments,' Harvard Journal of Asiatic Studies, 1937, Vol. 2, 1-3.

2. Biot, E., 'Mémoires sur divers minéraux chinois, appartenant à la collection du Jardin du Roi,' Journal Asiatique (3rd series), 1839, Vol. 8, 206-230.

This collection of around 80 minerals (now in Musée d'Histoire Naturelle, Paris) was assembled in south China in the 1720's or 1730's by J.F. Vandermonde, and is noted here because several pigment minerals are included: e.g., lead white, litharge, realgar, orpiment, green and blue copper carbonates, various iron oxides and earths. Identifications were by A. Brongniart, methods not stated. This source is historically useful since many of the samples are labelled with their Chinese names.

3. Cheng Te-k'un, 'The t'u-lu colour-containers of the Shang-Chou period,' Museum of Far Eastern Antiquities, Stockholm, Bulletin, 1965, Vol. 37, 239-250.

14 of these square vessels, each having four cylindrical receptacles, and recognized as colour containers, are described. Several of them contain residues; elements in the residues of one were identified by emission spectroscopy, with the results: green, copper compound; red, iron oxide; black, carbon; white, calcium compound. AATA, 6(1) E4-1.

4. Delbourgo, S.R., 'Two Far Eastern artifacts examined by scientific methods,' International Symposium on the Conservation and Restoration of Cultural Property - Conservation of Far Eastern Art Objects - Nov. 26-29, 1979, Tokyo, Tokyo National Research Institute of Cultural Properties, 1980, pp. 163-179.

One of the artifacts was a 9th-century painting from Tun-huang. The identifications (x-ray fluorescence)

were: blue, azurite; green, atacamite and parataca-
mite; reds, vermilion and red lead; brown, "burnt
ochre"; white, lead white; gold leaf. AATA $\underline{19}$-665.

5. FitzHugh, E.W., Zycherman, L.A., 'An early man-made
    blue pigment from China - barium copper silicate,'
    Studies in Conservation, 1983, Vol. 28, 15-23.

Sources were painted pottery objects from the Han
dynasty, and excavated coloured sticks dated (where
known) to the 5th-3rd century B.C. Identity with
$BaCuSi_4O_{10}$ was secured by x-ray diffraction. Also
present was a purple pigment, apparently containing
the same elements, but not completely identified.
AATA $\underline{20}$-731.

6. Gettens, R.J., 'Pigments in a wall painting from
    central China,' Technical Studies in the Field of
    Fine Arts, 1938, Vol. 7, 99-105.

The painting is from the Ming dynasty. Identifications
by microscopy and microchemistry gave the following:
white, white clay; black, carbon; red, vermilion;
orange-red, red lead; brown-red, iron oxide; yellow,
yellow ochre; green, malachite; blue, azurite. A
brown colour contained lead and may have been PbO_2.

Some cross sections were also studied.

7. Gettens, R.J., Feller, R.L., Chase, W.T., 'Vermilion
    and cinnabar,' Studies in Conservation, 1972, Vol.
    17, 45-69.

Four identifications of red HgS in oracle bones,
lacquer-work and a wall painting, are cited. Micro-
chemistry and x-ray diffraction were used. AATA $\underline{9}$-698

8. Gettens, R.J., Kühn, H., Chase, W.T., 'Lead white,'
    Studies in Conservation, 1967, Vol. 12(4), 125-
    139.

Around a half-dozen identifications of lead white in
various Chinese paintings, methods not generally
specified, are cited. AATA $\underline{7}$-1038

9. Moffatt, E., Adair, N., Young, G., 'The occurrence
    of oxalates on Chinese wall paintings,' Proceed-
    ings of the Fifth International Seminar, Applica-
    tions of Science in the Examination of Works of
    Art, 7-9 Sept. 1983, Boston Museum of Fine Arts,
    forthcoming.

This appeared as a poster session at the above Seminar
and is currently in press. The paintings in question
are from the Yüan dynasty and various pigments were
identified in the course of investigating an unusual
chemical deterioration.

10. Oguchi Hachirō, Hayashi Isao, 'On the coloring
    materials and painting techniques of artifacts
    unearthed from the tomb of the T'ang dynasty at
    Turfan,' Bulletin of the Department of Fine Arts,
    Tokyo University of Arts, 1981, Vol. 16, 1-40
    (Japanese, English summary).

A painting on silk and a painted wood sculpture were
investigated. Identifications, by x-ray spectra in
the electron microprobe, were: reds, vermilion and
haematite; yellow, goethite; green, malachite; blue,
azurite; whites, kaolin and calcium carbonate. An
organic yellow and an organic red were presumed to be
gamboge and lac dye respectively.

11. Shensi Province, Department of Cultural Relics and
    Provincial Museum, 'Cultural relics of the T'ang
    dynasty excavated from Ho-chia village in the
    southern suburbs of Hsi-an,' Wen Wu, 1972, No. 1,
    30-42 (Chinese).

A hoard excavated at the above location, probably buried
in A.D. 756, contained a number of mineral substances
described as "medicinals", and including, for example,
cinnabar, litharge, and pulverized gold. The presence
of labels adds historical importance. See also Hsia
Nai et al., New Archaeological Finds in China,
Foreign Languages Press, Peking, 1972, pp. 3-5.

12. Waley, A., section on 'Pigments' in the Introduc-
    tion to A Catalogue of Paintings recovered from
    Tun-huang by Sir Aurel Stein, London 1931, pp.
    xlvi-xlvii.

The paintings are dated to the 9th-10th centuries. The
results, obtained by "a technical chemist" by methods
not given except as noted, were: gold in powder form;
black, carbon; brown, bituminous earth; green, a
copper carbonate; blue, a copper carbonate; yellow,
orpiment; reds, iron oxide and vermilion (shown by
reduction to mercury); white, a calcium compound.

13. Wang Shou-tao, 'X-ray analysis of the pigments of a
    printed and colored gauze (N-5) from Han Tomb No.
    1 at Ma-wang-tui,' Hua-hsüen t'ung-pao, 1975, No.
    4, 246-249 (Chinese).

The colours on this silk fabric of the Han dynasty were
analyzed by x-ray diffraction. The following compounds
were found, sometimes as mixtures: red hexagonal
mercuric sulphide (cinnabar); black cubic mercuric
sulphide (black cinnabar); lead sulphide; sericite
(finely-divided mica) containing quartz. Carbon-based
ink was probably also present. AATA $\underline{13}$-338.

14. Warner, L., Buddhist Wall-paintings, a Study of a
    Ninth-century Grotto at Wan Fo Hsia, Harvard
    University Press, Cambridge, Massachusetts, 1938,
    pp. 9-11.

The author cites identifications by R.J. Gettens of
pigments used at Tun-huang (presumably also 9th century);
the methods are not given but probably involved
microchemistry. Listed are: black, carbon; whites,
kaolin and lead white; reds, vermilion, red ochre,
red lead and an organic red; yellow, an organic
yellow (probably gamboge); green, malachite; blues,
azurite and indigo.

15. Winter, J., '"Lead white" in Japanese paintings,'
    Studies in Conservation, 1981, Vol. 26, 89-101.

This paper is mostly about Japanese pigment history,
but describes also identifications (by x-ray diffrac-
tion) of basic lead carbonate on 12 Chinese paintings,
and of lead sulphate on one, the paintings dating
from the 10th-16th centuries. AATA $\underline{18}$-1458.

Section 20

Glass, Ceramics and Related Materials

Verres, céramiques et matériaux apparentés

MECHANICAL PROPERTIES OF SOME FILL MATERIALS FOR CERAMIC CONSERVATION

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Fig. 1

SUMMARY

Many different fill materials for ceramics have been used since the 19th century. However, very little scientific research has been carried out to assess their compatibility with the original ceramic and their subsequent behavior in various climatic conditions. For this reason, different fill materials in ceramic molds have been tested under adverse thermal conditions. Evaluations of other properties, such as workability, reversibility and health safety factors were also made. The results indicate thixotropic epoxy paste laminated with acrylic modeling paste possesses superior properties for fill materials.

Lacunae filling (or gap filling) of ceramics has been an object of discussion for a long time. A number of different techniques and materials have been employed but few have been precisely tested to determine their compatibility with the original material and their long range effectiveness. This fact is reflected in the available literature on ceramic conservation, most of which is limited to the scope of practical application, concerned primarily with such questions as workability, texture, ease of application, and reversibility.[1]

About six years ago, the Antiquities Conservation Laboratory of the J. Paul Getty Museum in California employed several new materials to fill and restore ancient ceramics. Although satisfactory results were obtained for a considerable time, it was decided to make comparative mechanical tests on these and similar materials under severe climatic conditions. This was desirable since the original objects might occasionally be subjected to extreme stress such as those in airplane cargo areas during transport, where the temperature could drop to −40°C and below. It was also useful to ascertain the behavior of the fills over long time periods in order to better choose the appropriate material, decreasing the chances of incurring unexpected damage in the future.

PROCEDURES AND RESULTS

The difference in coefficients of thermal expansion between synthetic filler and ceramic substrate is the most important factor of incompatibility. Therefore, the coefficients were determined for all materials involved, ceramic and fillers. The mechanical properties of some of the resins were modified by adding inert materials. The results are presented in Table 1.

Practical testing of filling materials in ceramics necessitates procedures that simulate actual conditions of use. These substances used to join ceramic fragments can exert tensile strain if the binder contraction is greater than that of the ceramic. To detect both tensile and compressive effects, ceramic molds were made and fired at 926°C. (Figure 1).[2]

The fill materials were chosen to represent a variety of substances used in conservation, ranging from plaster of paris (the standard of comparison due to its long and widespread use) to methacrylates and epoxies.[3] Since inert fillers, such as glass microspheres,
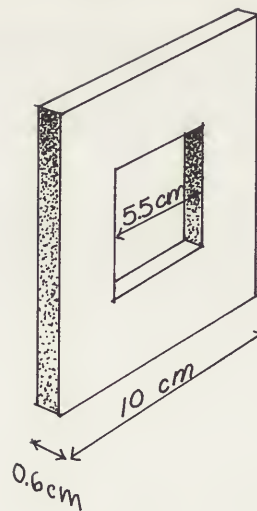
decrease the thermal expansion of polymers, they were added to several mixtures. Talc and mica were added, respectively, to one sample each.

The various materials were mixed in standard fashion and the inner edges of the ceramic mold cavity were wetted as thoroughly as possible prior to application. The bottom face of the smoothly sanded mold was covered with a sheet of Mylar, backed with 3 mm thick rubber and a 6 mm thick plywood square. These layers were held tightly to the ceramic mold with padded C-clamps.

Thermal shock testing was carried out by placing the filled molds in a Thermotron Environmental Chamber[4] programmed for increasingly severe cycles of temperature and rates of change. Details of the cycles and observations of the effects on fourteen fillers are listed in Table 2.

Cycle I was considered to be a rather rigorous test of compressive and tensile effects due to the difference in thermal expansion between the ceramic and adhesive. However, even after a total of 128 loops through this cycle and the somewhat more extreme Cycle II, no cracks or deterioration of any kind were noted in the test samples. Progressively lower temperatures, therefore, were used as the low limit in subsequent cycles. The rate of change was also decreased in the immediately succeeding cycles so that the lower temperature would be the primary determinant of any effect.

When the low temperature limit was changed to −10°C, the pure epoxy fillers, Araldite 504 and Ablebond 342-1, showed cracks after only 20 cycles. HXTAL NYL-1 and microsphere-filled epoxies were much more resistant to thermal shock, requiring many additional cycles at a very rapid rate of change. The methacrylate adhesives, filled or unfilled, showed intermediate resistance.

CONCLUSIONS

1. There is a large difference between the thermal expansivity of ceramics and all the tested fill materials, whether traditional or modern synthetics. However, early failure occurred only when a difference of greater than about 45 units in their thermal coefficients was present. All unfilled resins are therefore unacceptable for use, since they have coefficients 65 to 200 units greater than that of the ceramics. See Table 2.

2. Addition of inert materials to the resins, especially glass microspheres, lowers their coefficient of thermal expansion considerably, making them more resistant to thermal stress.

3. Three different patterns of damage appeared during the tests:

   a. The material pulled away from the ceramic after contraction due to poor adhesion.
   b. Damage caused by resin contraction, resulting in the tensile breakage of the test molds (Fig. 2).
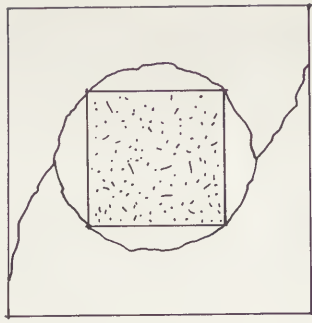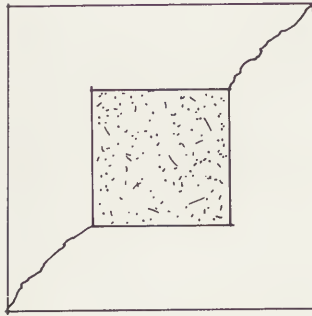
Fig. 2

Fig. 3

c. Damage caused by resin expansion, resulting in the diagonal breakage of the test molds (Fig. 3).

4. Four samples, plaster of paris, acrylic paste, and Ablebond epoxies filled with glass microspheres (1:1 and also 1:2.5), survived all the tests without damage. Only one tested material, acrylic paste, formed from acrylic polymer emulsion and calcium carbonate, remained unchanged after an extreme cycle with a temperature drop to -80°C.

5. All the samples were unaltered after the first two cycles, both designed to simulate long exposure to very detrimental museum conditions. This result indicates that any of the substances tested are thermally suitable for general ceramic application.

Additional important factors of reversibility, ease of application and health safety must be considered in selecting the fill material for practical use. The following combination was the preferred choice: a substrate of epoxy paste, a clay-like mixture of two components, laminated on both sides with acrylic modeling paste.

The epoxy is a 1:1 noncritical mixing rate system which may be dipped in water to facilitate kneading prior to application and is produced by Philadelphia Resins under the name of Pliacre. Some physical properties, according to the manufacturer, are: pot life - 45 minutes at 22°C; cure time - 16 hours at 22°C; hard set - 6 hours; shrinkage upon curing - undetectable (below 0.0001%); reversibility - with chlorinated hydrocarbons (methylene chloride), or temperatures of 70°-75° at which it become soft and easily removable with a scalpel.

Pliacre's working properties make it extremely easy to apply, being similar to modeling clay with a self-supporting thixotropic consistency. Its light gray color can be altered with either dry prigments or acrylic colors and its polyamide hardener is of low toxicity.

Pliacre's negative properties are those of yellowing and requiring slightly more effort to reverse than most traditional fillers. However, the first disadvantage is overcome by the technique of coating it with acrylic modeling paste.

The epoxy is applied to the ceramic by firmly pressing it on to the sides of the lacunae to be filled. The open space is bridged by a thin layer of the same material. If a temporary support is needed, a nonsticking polyethylene sheet provides an excellent barrier between the support and the Pliacre.

After some hardening has occurred, properly colored acrylic modeling paste is applied over both sides of the epoxy. Best results are obtainable with Liquitex modeling paste, applied with a palette knife and then smoothed with a potter's steel palette.

Liquitex, a white paste with 25% water content, has many advantageous properties; it is reversible in ketones, aromatics and to a lesser degree alcohols, easy to sand, and nonyellowing. However, it does have a significant disadvantage; acrylic modeling paste shrinks pronouncedly upon drying, causing undesirable cracks to form. To avoid this consequence, the desired thickness must be formed by laminating several thin layers.

Pliacre and Liquitex paste adhere very well to one another. The epoxy forms the skeleton and the paste forms an easily workable surface preventing yellowing of the Pliacre from exposure to light. The surface is worked with wet and dry sand paper to yield the final finish. Grit numbers 180, 240, 400, and 600 are used in this order for the best results. The finished surface provides an excellent base for all painting mediums.

The epoxy fill/acrylic finish combination has been successfully used for small fills as well as for very large reconstructions of fragmented pottery.

TABLE 1

Thermal Expansion Coefficients*

*Type of Material Specific Substance	Coefficient of Linear Thermal Expansion (in cm/cm °C x 10^{-6})
STRUCTURAL*	
Ancient ceramic (500 BC)	2
Present test ceramic	4
INORGANIC FILLER*	
Gypsum (from plaster of paris)	19
ORGANIC FILLER*	
Acrylic modeling paste	21
ADHESIVE POLYMER ACRYLIC*	
Polymethyl methacrylate (Technovit 4004)	97
Polymethyl methacrylate fumed silica (Technovit 4004 with Cab-O-Sil, 1:1 v/v)	78
Polymethyl methacrylate with glass microspheres (Technovit 4004 with 3-M Glass Bubbles 1:1 v/v)	40
Polymethyl methacrylate with glass microspheres and mica (Technovit 4004 with 3-M Glass Bubbles and mica 2:1:1 v/v)	71
EPOXY*	
Araldite 502	67 (below 35°C)
Araldite 502 with glass microspheres (1:2.5 v/v)	58 (below 49°C)
Pliacre (an epoxy probably filled with talc)	44 (below 45°C)

HXTAL NYL-1	71		Araldite 6010, foamed with PMHS, + magnesium trisilicate (1:1 v/v)	76 (below 37°C)
Ablebond 342-1	71			
Ablebond 342-1 with glass microspheres (1:1 v/v)	47		POLYESTER	
Ablebond 342-1 with glass microspheres (1:1.5 v/v)	34		Akemi	203

TABLE 2

THERMAL SHOCK TESTS ON FILL MATERIALS FOR CERAMIC CONSERVATION*,**

	Initial Temperature (1)	Time Held at (1)	Time to Cool to (2)	Temp. (2)	Time Held at (2)	Time to Warm to (2)	Comments
I.	30°C	1 Hr	1/2 Hr	10°C	1 Hr	1/2 Hr	Mild Thermal shock, repeated for 56 cycles. No effect noted (cracks, separation, etc.)
II.	35°C	1 Hr	1/2 Hr	5°C	1 Hr	1/2 Hr	Somewhat more vigorous conditions of thermal shock. No effects noted at 72 cycles.
III.	35°C	4 Hrs	8 Hrs	0°C	4 Hrs	8 Hrs	Lower temperature set to 0°C. Sample 6 showed one crack after one cycle. Other text samples showed no change after 11 2/3 cycles.
IV.	35°C	4 Hrs	10 Hrs	-10°C	4 Hrs	10 Hrs	Lower temperature set to -10°C. Slower cooling and warming cycle. After 10 cycles cracks appeared in samples 2 and 11.
V.	35°C	4 Hrs	4 Hrs	-10°C	4 Hrs	4 Hrs	More vigorous conditions of cooling and heating for 2 cycles. Samples 1,2,3,4,5, 6, and 11 showed minute cracks.
VI.	35°C	4 Hrs	2 Hrs	-10°C	4 Hrs	2 Hrs	Even more vigorous cooling-heating conditions for 20 cycles. Samples 9 and 10 cracked here.
VII.	35°C	4 Hrs	1/2 Hr	-10°C	4 Hrs	1/2 Hr	More extreme temperatures range with rapid cooling-heating conditions for 8 cycles. Only test samples 7,8,12 and 13 did not show cracks.

TABLE 2 SUMMARY: Sample 6 showed early failure (after beginning of Cycle III). Samples 2 and 11 failed next under rather rigorous conditions. Samples 1,3,4,5,9 and 10 failed when the rate of cooling and heating was increased. Sample 13 failed only when such rates became very rapid. Samples 7, 8, 12, and 13 resisted not only temperature extremes of 40°C and -20°C, but cooling and heating rates that were excessively fast.

*Square ceramic tiles (0. cm thick and 9.9 x 9.9 cm), from which inner squares (5.5 x 5.5 cm) had removed, were fired at 926°C. The inner space was filled with the adhesive and, after drying or curing at room temperature, the test pieces were placed in a Thermotron SM16C Environmental Chamber and were thermally cycled in the above described manner.

**Identification of samples:

Sample No.	Type	Brand
1.	Methacrylate	Technovit 4004
2.	Epoxy	Araldite 502
3.	Epoxy	Araldite 502 + Glass Spheres (1:1 v/v)
4.	Epoxy	Araldite 502 + Glass Spheres (1:2.5 v/v)
5.	Methacrylate	Technovit 4004 + Glass Spheres (1:1 v/v)
6.	Methacrylate	Technovit 4004 + Glass Spheres + Mica (2:1:1 v/v)
7.	Gypsum	
8.	Acrylic	Modeling Paste ("Liquitex")
9.	Epoxy	Pliacre
10.	Epoxy	HXTAL NYL-1
11.	Epoxy	Ablebond 342-1
12.	Epoxy	Ablebond 342-1 + Glass Spheres (1:1 v/v)
13.	Epoxy	Ablebond 342-1 + Glass Spheres (1:2.5 v/v)
14.	Epoxy Foam	Araldite 6010 + Magnesium Trisilicate (1:1 v/v) (foamed with PMHS)

List of Manufacturers

1. Ablebond 342-1   Ablestik Laboratories
        833 W. 182 Street
        Gardenia, Ca. 90248

2. HXTAL NYL-1   Hillery Enterprises
        1909 Richcreek Road
        Austin, Texas 78757

3. Araldite 502   CIBA-Ceigy Corp.
        3 Skyline Drive
        Hawthorne, N.Y. 10532

4. Akemi Trans-   Wood & Stone, Inc.
   parent flowing   7567 Gary Road
        Manassas, Va. 22110

5. Technovit 4004   Kulzer & Co. GMbH
        Phillip-Reis - Str.8,
        D-6393, Wehrheim 1,
        Germany

6. Pliacre   Philadelphia Resins Corp.
        20 Commerce Drive
        Montgomeryville, Pa. 18936

7. Liquitex   Binney and Smith, Inc.
        Easton, Pa. 18042

8. Glass microspheres   "3M" Corporation
        223-2 3M Center
        St. Paul, Minn. 55101

Footnotes:

1. See attached bibliography.

2. Composition: Red earthware (30%), sand (20% of 30 mesh), soapstone (30%) and feldspar (10%). Minimum shrinkage 6%, water absorption, 17%. Supplied by Custom Ceramic, Malibu, Ca. 90265

3. Details of ratios:

Resin	Catalyst	Proportion R/C by weight
Ablebond 342-1 Part A	Part B	100:32
HXTAL NYL-1 Part A	Part B	100:32
Araldite 502	Araldite 956	100:20
Akemi Trans- parent flowing	Benzoyl Peroxide	See Mfr. spec (15:0.3)
Technovit 4004 (Liquid)	Technovit 4004 (Powder)	100:100
Pliacre Part A	Pliacre Part B	1:1

4. Thermotron Industries, Inc., Holland, Michigan 49423.

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12. Vlad Borrelly, L., 'Materiali Ceramici', Problemi di Conservazione, ed. Giovanni Urbani, Editrice Compositori, Bologne (1980) 63-72.

13. White, Muriel, Restoring Fine China, Larousse and Co. Inc. (1980).

THE EVALUATION OF SOME POLYESTER AND EPOXY
RESINS USED IN THE CONSERVATION OF GLASS

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SUMMARY

Following a search of the conservation, resins
and adhesives literature twelve resins des-
cribed as water white were obtained for evalu-
ation. Of these, four were in fact highly
coloured when cured and unsuitable for use in
the conservation of glass. Experimental work
was carried out on the eight remaining pro-
ducts - four epoxy resins and four polyester
resins. Colour stability on exposure to heat
and light, reversibility, shrinkage, gap
filling and adhesive properties were investi-
gated. The most suitable resin for gap fill-
ing was found to be vosschemie polyester resin
and the most suitable adhesive was Ablebond
342-1.

1   INTRODUCTION

In the conservation of glass, epoxy resins are
often used for edge to edge joining and poly-
ester resins for gap filling. Ideally these
resins should be water white, exhibit good
stability to light and heat, low shrinage on
curing and be reversible. Commercial resins
described as water white in the technical
literature are often yellow. Sometimes a thin
film is apparently water white whereas a
thicker section for gap filling appears
yellow.

A search of the conservation literature (1-7)
and the resins and adhesives literature was
made, and 12 resins described as water white
chosen for investigation. Samples were
obtained. Of these, 4 resins were highly
coloured when mixed and cured, but further
experimental work was carried out on the
remaining 8 products - 4 epoxy and 4 poly-
ester resins. The epoxy resins are Ablebond
342-1, Eccocoat 1540, Eccobond 24 and Plasto-
gen EP. The polyester resins were Metset
Resin 'SW', Tiranti clear polyester embedding
resin (pre-acceterated), Trylon clear embedd-
ing resin EM 306AP and Vosschemie Polyester
resin.

2   EXPERIMENTAL

Samples of cured resins were prepared and used
to determine colour stability on exposure to
heat and light, reversibility and shrinkage.
The gap filling and adhesive properties of the
resins were also investigated.

2.1   Preparation of resin samples

The resins were prepared according to the
manufacturers' recommendations. Those mixed
by volume were measured out in graduated
pipettes and those mixed by weight were
weighed to two decimal placed. The catalysts
and hardeners supplied in custom made dropping

bottles were measured out using the recommen-
ded number of drops from the bottle. Mixing
proportions are given in Table 1.

TABLE 1		
Resin	Mixing proportions	
	resin	hardener/ catalyst
Ablebond 342-1	100 parts	32 parts (b w)
Eccobond 24	4 parts	1 part (b w)
Eccocoat 1540	10 parts	4 parts (b w)
Plastogen EP	10 parts	3 parts (b w)
Metset 'SW'	20 mls	5 drops
Tiranti	100 mls	3 drops
Trylon EM 306PA	50 g	1 ml
Vosschemie	20 g	5 drops

An attempt to prepare thin films for reversi-
bility, heat and light ageing studies was
abandoned because the polyester resins did not
cure when pressed between sheets of polythene.
To produce comparable samples of all the
resins, blocks of resins were case in poly-
thene moulds. The blocks were cut into discs
of 0.5 cm thickness on a lathe and then
polished on metallurgical polishing wheels,
using diamond polishing paste.

2.2   Heat ageing

Samples were aged at 70°C for 28 days in an
oven. The colour of the samples before and
after ageing was determined by comparison with
the Methuen Handbook of Colour (8). The infra-
red (IR) spectra and ultra violet (UV) -
visible spectra of the samples were measured
before and after ageing.

2.3   Light ageing

Light ageing was carried out using a Microscal
light fastness apparatus, with a 500 watt MBTL
lamp (10). the UV-visible spectra of the pre-
pared resin samples were measured prior to
exposure. They were then mounted together
with a sample of ISO blue wool standard 6, (9),
in a water cooled cell to reduce the heating
effects of the lamp and exposed until the
first of the resins yellowed perceptibly.
Following light ageing the UV-visible spectra
of the resins were remeasured.

2.4   Reversibility

The solubility of heat aged, light aged and
unaged resin samples was determined in 5 common
solvents: acetone, industrial methylated
spirit (IMS), trichloroethane, Desolv (a pro-
prietry solvent for epoxy resins) and acetone
based Nitromors (a proprietry paint stripper).
Sufficient solven to produce a 10% solution
was added to an accurately weighed sample of
cured resin in a sealed tube. After 24 hours
the solvents were carefully removed and the
insoluble material dried to constant weight in
a vacuum oven. Percentage weight loss based
on the original weight of the sample was cal-
culated.

2.5 Shrinkage

The resins were mixed and cast in a cylindrical metal mould of known internal diameter. The samples were allowed to cure for 72 hours before removal. The diameter of the blocks was then measured using a micrometer until it became constant. A graph of percentage linear shrinkage against time was plotted.

3 RESULTS

3.1 Preparation

Most of the 8 resins were easy to mix. A large number of air bubbles were produced when Eccobond 24 and Eccocoat 1540 epoxy resins and Vosschemie a polyester were mixed. Eccobond 24 had a grey/blue tinge, Eccocoat 1540 a yellowish tinge and Metset 'SW' a pink tinge. the other materials were water white. During curing the Vosschemie resin turned bright green and then became colourless again.

3.2 Heat ageing

The colour of each sample was determined by comparison with the Methuen Handbook of colour. the colour coordinates are given in Table 2.

Figure (1) Heat-aged Vosschemie

TABLE 2		
	colour coordinates	
Resin	Unaged	aged 70°C for 28 days
Ablebond 342-1	1A1	4B7
Eccobond 24	20A2	4B6
Eccocoat 1540	1A2	3A2
Plastogen EP	1A1	4A2
Metset 'SW'	1A1	4A2
Tiranti	1A1	4A2
Trylon EM 306PA	1A1	2A2
Vosschemie	1A1	1A2
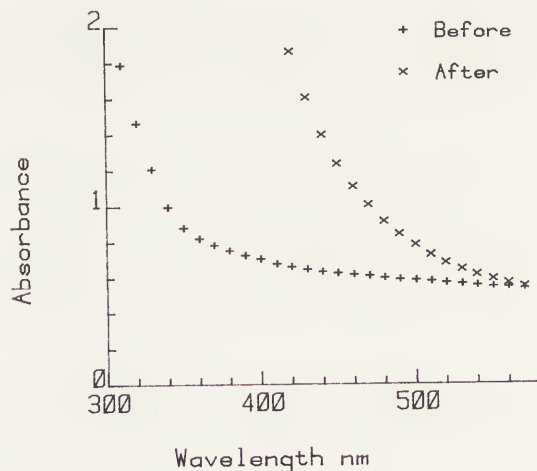
Figure (2) Heat-aged Ablebond

All of the epoxy resin samples darkened to shades of amber during heat ageing. The greatest darkening occuring with Ablebond 342-1. The polyester resins became slightly yellowish during heat ageing. The least change in colour occured with the water white Vosschemie resin. It can be seen that the polyester resins show much greater colour stability at the elevated temperature than the epoxy resins.

A change in the UV/visible spectrum of the resins occured on heat ageing. This change was greatest for the epoxy resin Ablebond 342-1 and least for Vosschemie polyester resin. Generally least change was observed for the polyester resins. Typical spectra obtained before and after ageing for Ablebond 342-1 and Vosschemie are shown in Figures 1 and 2.

3.3 Light ageing

The blue wool standard 6 was perceptibly faded after 158 hours exposure to the MBTL lamp. At this time there was little change in colour of any of the resins and the exposure was continued until more yellowing occurred. After 2300 hours of exposure, the colours of the samples were assessed using the Methuen Handbook of Colour and are given in Table 3.

TABLE 3			
	Colour coordinates		
Resin	Unaged	Aged	
		758 h	2308 h
Ablebond 342-1	1A1	1A1	1A1
Eccobond 24	20A2	4A6	4B6
Eccocoat 1540	1A1	4A3	4A4
Plastogen EP	1A1	3A2	3A3
Metset 'SW'	1A1	1A2	2A2
Tiranti	1A1	1A2	2A3
Trylon EM 306AP	1A1	1A2	2A3
Vosschemie	1A1	1A1	1A1½

With the exception of Ablebond 342-1 the epoxy
resins yellowed considerably more than the
polyester resins. Vosschemie polyester resin
was most stable to light ageing and the UV/
visible spectrum of this resin showed very
little change. typical spectra before and
after ageing for Plastogen EP and Vosschemie
are shown in figures 3 and 4.

Figure (4) Light-aged Plastogen

Exposure of Ablebond 342-1 and Vosschemie
resins to the MBTL lamp was continued until the
total exposure of 4000 hours was achieved.
During this period the Ablebond yellowed
slightly (Methuen coordinate 2A2) and the Voss-
chemie remained water white (Methuen coordinate
1A1½).

3.4   Reversibility

None of the samples were extensively soluble
in the solvents. The unaged polyester resins
were readily broken down in acetone, Desolv
and Nitromors, although only 19-24% of such
sample dissolved. The epoxy resins merely
broke up in Desolv and Nitromors with 12-13%
of each sample dissolving. Heat and light
ageing slightly reduced the solubility of some
of the resins, Eccobond 24 and Eccocoat 1540
being particularly affected.

3.5   Shrinkage

A graph of % linear shrinkage v time was pre-
pared for each resin. Representative curves
are shown in Figure 5, from these curves it
can be seen that the polyester resins shrank
much more than the epoxy resins.

Figure (3) Light-aged Vosschemie
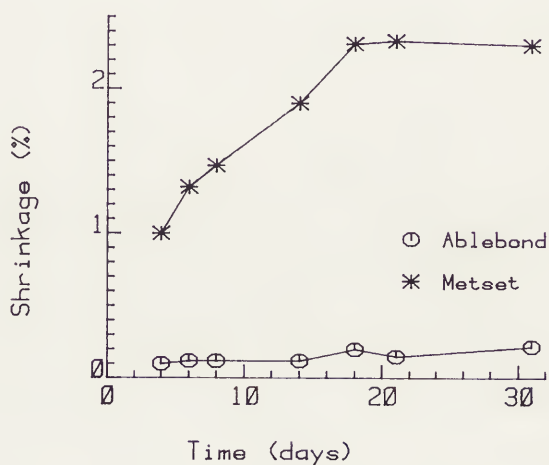
Figure (5) Linear Shrinkage

4 GAP FILLING AND ADHESION

4.1 Gap filling

Gap filling with all the resins was investigated using microscope slides. A mould was prepared by folding a sheet of Melinex (polyethylene terephthalate film) around two 75 x 25 mm microscope slides held 25 mm apart. The Melinex was attached to the microscope slides with adhesive tape and a second pair of microscope slides were taped on each side of the Melinex to provide rigid support (figure 6).
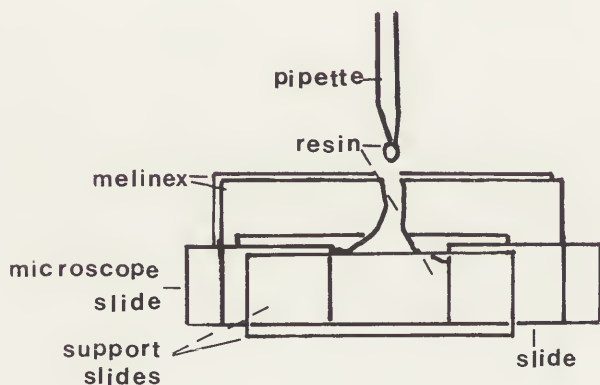
Figure (6)

Resin was run into the gap from a dripping pipette. The moulds were held in a bench-vice for 48 hours, after which the supporting microscope slides were removed. The Melinex sheet peeled away from the cured resin. The average dimensions of each gap filling was 25 mm x 25 mm x 1 mm. Both the epoxy and polyester resins formed satisfactory fills. In all cases the bond to the glass was firm and not broken by slight flexing of the assembly.

4.2 Adhesion

The adhesive properties of the resins were investigated by the joining of two microscope slides end on to simulate a break. The slides were cleaned with acetone laid end to end and joined with adhesive tape to provide support. A drop of resin was applied to one end of the joint and was drawn along the joint by capillary action. The assembly was left for seven days to ensure complete curing. The joined slides were then lifted by one end to determine whether the join was strong enough to support the weight of one microscope slide.

Trylon, Metset 'SW' and Tiranti polyester resins would not support the weight of the microscope slide because curing had been inhibited and the resin was still tacky. This was due to oxygen inhibition of the resin surface, a built-in feature of embedding resins. Vosschemie was the only polyester resins to fully cure and bear the weight of the microscope slide. All the epoxy resins cured and joined the slides satisfactorily. The strongest bonds were produced by Ablebond and Plastogen EP.

CONCLUSIONS

The polyester resins showed good colour stability when subjected to heat and light ageing. The Vosschemie resin being particularly stable. All of the epoxy resins yellowed considerably on heat ageing and Ablebond 342-1 was the only epoxy tested to exhibit good stability to light ageing.

None of the resins was completely soluble, but joins and gap fills could be broken down by immersion in solvents which caused the resins to swell and fragment. However if the glass were thin and weak such a process could cause more damage to the object.

Although both the polyesters and epoxies were capable of effectively bonding glass when used as gap-fillers, only the epoxies formed strong bonds when used to make joints. The bond formed when Vosschemie resin was used in this manner was weak compared with the strength of the epoxy bonds.

Metset 'SW', Trylon EM 306PA and Tiranti clear embedding resin formed good gap fills. Only one edge of the relatively large volume of resin was exposed to air and this was the only surface where curing was inhibited by oxygen. The edge was therefore tacky. When these resins are used to make a join a small volume is used and a proportionately large surface area is in contact with the air. Curing is therefore inhibited.

Because the Vosschemie polyester resin is very stable to light and heat, it is the most suitable, of the resins tested, for use in gap filling. Ablebond 342-1 is stable to light, but not to heat ageing. Of the epoxy resins investigated it is the most suitable for use as a jointing adhesive.

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De-Solve 292

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Nitromors

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MATERIALS SUPPLIERS

Ablebond 342-1

Intersem Ltd
Haywood House
PINNER
Middlesex   HA5 5QA
England

Eccobond 24 and Eccocoat 1540

Emerson and Cuming (UK Ltd)
One South Park Road
SCUNTHORPE
South Humberside   DN17 2BY
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Plastogen EP

Frnak W Joel Ltd
Oldmedow Road
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Metset Resin 'SW'

Metaserv
Metallurgical Services Labs Ltd
Reliant Works
Brockham
BETCHWORTH
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England

Tiranti Clear Polyester Embedding Resin

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Trylon Clear Embedding Resin EM306PA

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Vosschemie Polyester Resin

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UETERSEN
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A PRELIMINARY STUDY ON THE PRESERVATION OF SOME SELJUK CERAMICS BY γ -RAY INDUCED POLYMERIZATION

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SUMMARY

It is now very well known that high energy radiation (X or γ - rays) can initiate and control polymerization of some monomers impregnated in porous objects. In the present work this method of preservation is applied to some XIIIth century ceramics belonging to the Seljuk Period found in South-East Anatolia. Monomer impregnation is restricted to the surfaces of the object. The colored figures, drawings and structures which are present but not perceptible due to the erosion of the glaze on these objects become fully apparent upon polymerizing hydrophilic monomers on their surfaces. Although it is possible to obtain a soluble polymeric layer by carefully controlling the irradiation conditions,permanent protection of the substrate material can also be achieved by longer irradiation of the top polymeric layer.

INTRODUCTION

Many systematic studies have been carried out during the last decade, especially in France in the use of γ -rays for the conservation of works of art (1,2). The deep penetration and sterilizing action of γ -rays together with their ability to initiate and control the polymerization of monomers can be used simultaneously in the conservation and consolidation processes (3). This technique is being employed industrially in polymer technology in the preparation of wood-plastic combinations and in concrete-polymer materials.

This method has also been applied satisfactorily in our laboratories to the consolidation of some extremely degraded wooden objects and fossils found in Central Anatolia (4). In this paper we report the results of similar preservation studies now extended to ceramic objects.

EXPERIMENTAL

Ceramic objects used in this study are the parts of some vessels used in everyday life during the XIIIth century and were found in Samsat, an old Seljuk town near Adiyaman in South-East Anatolia (5). These objects had eroded surfaces which were contaminated with some soil. They were cleaned superficially by gentle and careful brushing taking care to avoid any over-cleaning.

For the surface treatments of these ceramic fragments different types of hydrophilic monomers were used as received from manufacturing companies. No attempt was made to free them from their inhibitors. Monomers were applied only to the surfaces of these objects in a dropwise manner. Among different monomers tested, hydroxyethyl methacrylate, hydroxypropyl methacrylate, vinyl acetate and some acrylic acid derivatives gave satisfactory results. To achieve a crosslinked polymer layer, small amounts of crosslinking agents were also added to some of the monomers.

Irradiations were carried out in a Gammacell 220, a ^{60}Co γ -irradiator at room temperature in air at a dose rate of 2.88 kGy/h. The conventional ferrous ferric (Fricke) dosimeter was used for dose rate measurements.

RESULTS AND DISCUSSION

The ceramic samples used in our previous work were impregnated with certain monomers and then irradiated with γ -rays to achieve polymerization within the object. This was observed to be a rapid method of increasing the mechanical resistance of the samples against shocks, etc. In this case however, the main aim of the study was not only to consolidate the objects but also to reveal the designs which were obscured by weathering.

The ceramic samples to be preserved in this study were badly degraded. Probably due to the very severe conditions to which these pieces were subjected, the glaze forming the top protective layer had partly or totally disappeared. This also resulted in the disappearance of colors and some figures protected by this layer. In certain parts of the surfaces where the glaze is retained, the underlying colored figures can still be seen, Fig. 1. When the surfaces of these pieces are wetted with water the figures become apparent with their full colors.This disappearance is probably due to the partial or total loss of the water of hydration of the inorganic dyes or pigments used during the preparation of these objects. The appearance of colors can be made permanent by covering the surfaces with a thin hydrophilic polymer layer. A polymer film can be obtained either by applying a polymer solution on the surfaces of these objects and letting the solvent to evaporate, leaving a film behind or by applying the monomers to the surfaces and carrying out the polymerization in situ. The latter method proved to be a successful one. Among different monomers tested, hydroxyethyl methacrylate, hydroxypropyl methacrylate,vinyl acetate and some acrylic acid derivatives gave positive results. These monomers were applied to the surfaces of the artefacts and they were then irradiated with γ -rays.

The final effects of such a treatment on the ceramic samples are very clearly illustrated in Fig. 1. The drawings and the colors which are not discernible on the untreated samples are fully visible and permanent on the treated ones. If the colored parts still remaining on the untreated ceramics shown in Fig. 1 a are closely examined it can be seen that the colors developed on the other parts of the objects upon this treatment are exact reproductions of the original tones.

(a)   (b)

(a)   (b)

Fig. 1. The photographs of ceramic objects before and after preservation by the γ-ray induced polymerization technique. a) Samples as received, before treatment; b) After treatment.

By a careful control of the irradiation conditions it is possible to obtain polymers which can later be removed by treatment with a suitable solvent. Irradiations to doses above that required for polymerization however, results in the crosslinking of the polymer chains. This is the case with vinyl acetate and acrylic acid derivatives. In the case of poly(hydroxyethyl methacrylate) and poly(hydroxypropyl methacrylate) the crosslinking of polymer chains is achieved with the addition of small amounts of crosslinking agents. This crosslinked layer provides a permanent protection for the substrate material. Repeated washings of objects revealed the insolubility of crosslinked polymer layer. This can be considered to be a permanent and long-term protection process especially for surfaces which are subject to deterioration as in the case of outdoor exhibitions.

Previous investigations of poly(acrylic acid)-alumina systems have demonstrated that there is a strong interaction between the polymer chains and alunina particles. It is also proposed that this interaction originates with the adsorption of acrylic acid on the surface of alumina prior to polymerization(6). An interaction of this type is likely to enhance the binding of acrylic polymers onto the surface of ceramic objects. Similar interactions can also be expected for poly(hydroxyethyl methacrylate) and poly(hydroxypropyl methacrylate) due to the presence of hydroxyl groups in the repeating units of these polymers.

According to Daniels(7), an ideal method of preservation should fulfill the following requirements:

1) The information potentially obtainable from the objects should not be lost.

2) The object should have an aesthetic appearance.

3) The substances used in conservation should not do any harm to the subject.

4) The preserved object should be easily handled.

5) The chemicals used in the conservation process should be easily removable.

The method proposed satisfies the first four of these requirements. Although it is not a prime aim of this work for the time being, it is also possible to perform this process reversibly by close control of the polymerization of the adsorbed monomers. When crosslinking and insolubilization of the polymer layer is wanted, this is very simply accomplished by irradiating the objects for longer periods. In order to apply this technique of preservation on a large scale, some further tests on the aging and discoloring behavior and on some other side reactions that may develop in the polymer layer are in progress.

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RESTORATION OF GLASS ANTIQUITIES

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SUMMARY

The conservation of glass antiquities may include several different processes: examination, cleaning, joining, filling or supporting, and cosmetic treatments. It is essential to examine the object carefully before deciding upon the best treatment as, in each case, the strength of the glass will determine the most suitable method of conservation. At the present time the methods used to repair glass are continually being developed with the availability of new materials. Synthetic resins which resemble glass in clarity have greatly improved the aesthetic appearance of repaired glass. According to their properties, these plastics may be used as adhesives, they may be cast into a mould to replace missing areas of glass or, in sheet form, they may provide support for isolated fragments of glass. The success of the restoration depends not only upon the artistic ability of the conservator but, until products are developed specifically for conservation purposes, on the imaginative use of materials that are available on the market today.

1. INTRODUCTION

This paper describes the materials and outlines some of the methods used to repair and restore glass antiquities. The main problems encountered when repairing glass are that:

(i) glass is difficult to bond because it is a highly polar material and the broken edges are often smooth and non-porous.

(ii) glass is subject to decay which, when advanced, leaves the glass in an extremely fragile condition, so that when broken it may be impossible to handle the fragments without causing further damage.

(iii) the refractive index (R.I.) of every glass varies with its composition, and it is problematic to match the R.I. of adhesives to that of glasses (1). Thus it is virtually impossible to 'lose' the cracks and break edges as in the case of ceramic restoration. However, some adhesives will fortuitously disguise cracks owing to their R.I. being close to that of glass, e.g. Ablebond 342-1 epoxy for lead glass.

(iv) the appearance of every glass antiquity is unique, and however skilful the work, the restoration will be unacceptable unless it is aesthetically pleasing (i.e. the restoration resembles the original glass).

However, some synthetic resins available at present will bond with, and do resemble glass in appearance. Modern moulding materials are more versatile and sensitive to detail than the plaster of Paris and waxes formerly used for glass restoration.

The success of a particular restoration depends upon the correct choice of resin, moulding materials and method. For each antiquity the condition of the glass, The shape of the object and the amount remaining, will determine the method of restoration chosen.

2. CLEANING

Historic glass in sound condition may be immersed in distilled water with few a drops of Synperonic NDB non-ionic detergent. A plastic bowl should be used on a bench, or foam plastic used to line a sink which should not have protruding taps. One piece of glass should be washed at a time and, after rinsing, should be allowed to dry naturally on soft paper towelling. An ultrasonic tank may be used to remove dirt trapped in folded rims or from inside narrow-necked vessels. Archaeological glass should not be immersed, but when in good condition can be cleaned with cotton wool swabs moistened with distilled water and Synperonic NDB. Where the surface of the glass is friable a soft sable brush should be used instead of cotton wool, which may catch on loose flakes and pull them off. If there is an inherent imbalance of alkali in the glass (2), for example Venetian glass and early English lead glass, it may be prone to weeping in humid conditions. Such glass is actually breaking down in the presence of moisture and therefore, after washing in distilled water to remove dirt adhering to the tacky surface, it should be dried through industrial methylated spirits and stored at a relative humidity of 42-45%.

Before attempting any treatment the glass should be carefully examined. Fragile glass or glass which has flaking decoration, should be consolidated only when absolutely necessary (3). As the glass will continue to be affected by moisture in the air, the movement of salts in the glass may cause a consolidated layer or lacquered surface to be pushed off. No consolidant has so far proved to be sufficiently permeable to moisture, as well as clear, colour-fast and stable. Where the glass is in immediate danger, Paraloid B72 diluted in toluene may be used. However it is usually preferable to store the glass in a stable environment than to apply any consolidant which, for practical purposes, may be considered to be irreversible.

3. REPAIR

The adhesive chosen to repair a glass antiquity depends on the strength of the glass. The adhesive must be capable of joining the pieces together satisfactorily, it must be chemically stable and not break down causing the object to fall apart, and yet it must remain reversible. Depending upon the method chosen to join the fragments of glass, the adhesive may be required to be viscous or highly mobile. Many adhesives have been tested for use with glass (4) the most successful have proved to be epoxy resins (e.g. Ablebond 342-1, HXTAL NYL-1 (5)) and the cellulose nitrate adhesives HMG and Durofix. Cyanoacrylates and UV curing acrylics have been used for repairing glass but their long term stability cannot be guaranteed.

Sound glass is usually repaired using an epoxy resin. The object may be assembled piece by piece using a very viscous resin e.g. Super Epoxy; but more commonly it is reconstructed without adhesive (6), the fragments being held together by small pieces of pressure-sensitive tape. A highly mobile resin such as Ablebond 342-1 is then introduced to the joins, along which it spreads by capillary action. Both thick and thin glass may be repaired by this method. Very small fragments of glass which cannot be easily taped, or glass which has a painted or gilded surface may be assembled by tacking the pieces together using small drops of a cyanoacrylate adhesive such as Cyanolit or Super Glue 3. An epoxy resin is then used as described above.

Epoxy resins are insoluble but can be removed with methylene chloride which causes the adhesive to swell and the fragments to part. For this reason it is inadvisable to use epoxy resins on fragile archaeological glass, which may be damaged by the swelling action. A cellulose nitrate adhesive, for example HMG, is preferred for decayed glass, glass with

flaking decoration, or in the case of a double-walled vessel where a mobile resin would flow in between the two glasses.

In a situation where an adhesive alone is not strong enough to support the glass, for example a broken wine-glass stem, it may be necessary to insert a dowel (7). Perspex rod (poly-methyl methacrylate) or glass rod is inserted with resin in small holes drilled into the two sections of the stem. This procedure will strengthen the join, and the vessel may be safely handled and displayed.

4. RESTORATION

Where a vessel is incomplete, i.e. part of the body is missing, it may be necessary to replace that area by casting with a liquid resin or shaping a pre-formed plastic sheet, or by supporting the fragments on a mount of glass or plastic.

4.1. Casting materials

There is a wide variety of polyester resins available which resemble glass in clarity (8, 9). These are liquid, colourless to a certain degree, and may be poured into a mould where they cure *in situ*. Clear embedding resins e.g. those made by the firms Vosschemie, Tiranti and Trylon, have good resistance to yellowing in light, and may be tinted wherever necessary to match coloured glass, using translucent polyester pigments. One disadvantage of using the polyester embedding resins is that the surface exposed to the air will remain tacky and therefore the resins must always be poured into a closed mould. Polyester laminating resins will harden in an open mould without tackiness but, because they lack the mechanical strength of the embedding resins, they must be reinforced with fine surface glass tissue.

Preformed poly-methyl methacrylates such as Perspex, are clear and have good light-fastness properties. They are thermoplastic and are available in sheet or rod form. However the use of sheet acrylic to replace glass from the body of a vessel is very time-consuming and requires accuracy in cutting and filing. Some poly-methyl methacrylates are available in liquid form (10) and can be cast in open or closed moulds. Technovit 4004a which is opaque, may be used to restore translucent or coloured glass. This resin also has the advantage that, being thermoplastic, it can be cast as a simple form which can then be heated and bent to produce a more complex shape.

4.2. Moulding materials

When a mould is to be taken from a remaining section of the object, the choice of moulding material will again depend upon the strength of the glass. The most useful materials for mould-making are sheet dental wax and various grades of silicone rubber. Dental wax is inexpensive, and easy to handle and to remove from the glass after the casting operation. Silicone rubber e.g. Silcoset 105, Silastic RTV 501 and Rhodosil 11504A are much more expensive than wax, and are more difficult to use in that they are liquid, but they can reproduce very fine details and, as they are flexible when cured, can be used to mould intricate shapes in one piece. If necessary silicone oils may be added to the rubber to make it more mobile; or it may be thickened by the addition of fumed silica.

4.3. Mounting the glass

Moulding and casting in missing areas of glass is not always possible or desirable when most of the vessel is missing, or where the glass is extremely friable. High-silica glass tubes can be heated and reshaped to form supports for isolated glass fragments, thus holding them in their correct positions relative to each other (11). Careful measurements are taken from the interior of the vessel, and tubes of glass mounted on a lathe, heated to a very high temperature, and blown to the exact shape required. This process, known as lampworking, is exacting, and few museums have the facilities for this type of restoration. however,

acrylic sheet may be shaped by vacuum forming to fit inside a broken vessel thus producing an aesthetically pleasing mount for the fragments.

When a glass antiquity is restored, the areas replaced are normally matched in colour to the original, but are left undecorated. As previously mentioned, it would be normally impossible to restore glass invisibly; and to replace missing decoration such as gilding or enamelling on the original, would be considered unethical. In cases such as these, it may be possible to improve the appearance by cosmetic treatment. For example, plastic acetate film e.g. Scotchtint which is available in various shades of silver and gold, may be placed behind a mirror to simulate missing areas of silvering. The loss of enamel on "zwischengoldglas" has been similarly disguised (12) by copying the enamel decoration onto a sheet of thin plastic fitted around the glass.

5. CASE HISTORIES

Where the missing area of glass is very small or the interior of the vessel is inaccessible, a one-sided wax mould can be easily made and fixed behind the void. Epoxy resin can then be used to form the cast. This type of mould can also be used where the glass is too thin to withstand moulds being taken off both sides: fibre glass tissue and polyester laminating resin being used to fill the void.

Simple shapes are more quickly and cheaply moulded using wax, and it is often safer to use a wax rather than a silicone rubber mould on gilded or friable surfaces, as, after casting the resin, the wax may be easily removed from the glass with warm air, whereas the rubber mould adheres strongly. However, when the glass is sound and the missing areas are too complicated to be moulded using wax, silicone rubber may be safely used.

Clear polyester resin is used for preference to form the cast when an enclosed mould can be made; and, using a syringe, the resin may be introduced through a small hole in the silicone rubber. The mould can be taken off the original where it is the same shape as the missing part, but where the area to be replaced is not matched anywhere else on the object, a model must be made of it. The modelling material chosen, for example Aloplast or fine potters' clay, should be compatible with the silicone rubber. When taking a rubber mould from a simple shape a one piece mould may be adequate; but a piece mould is required for an extremely complicated or large area, undercuts, or where the interior of a vessel is inaccessible. Piece moulds may be supported by a plaster of Paris or a resin and fibreglass mother mould (case mould) if necessary.

Where the clarity of the resin cast is not essential, another technique may be used as an alternative to modelling (8), and takes advantage of the thermoplastic property of poly-methyl methacrylates, for example Technovit 4004a. A simple acrylic cast can be heated in boiling water until pliable, reshaped by hand and cooled quickly when it will retain its new shape. In this way handles, missing ornaments etc. may be reproduced without using a time-consuming modelling technique.

Finally, a resin cast can be polished using a fine abrasive paste such as Solvol Autosol on a rotating buff. Alternatively where the glass is decayed and therefore not highly reflective, the cast may be abraded to complement the original.

Cone beaker, British Museum

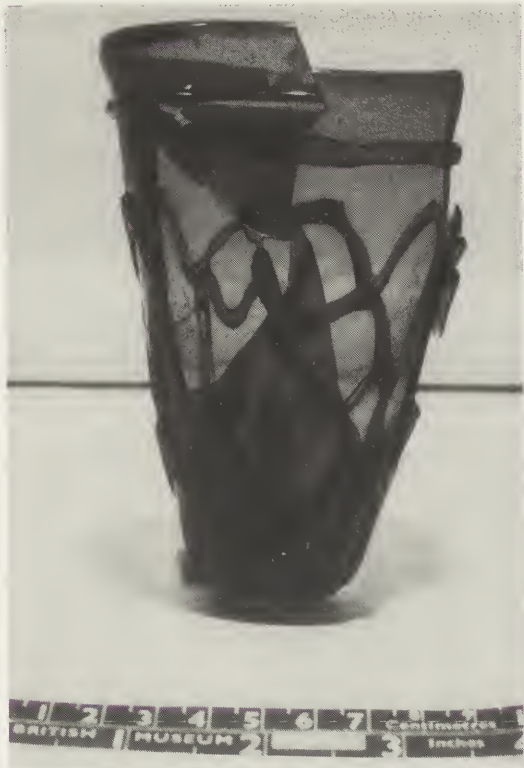Fragments assembled using epoxy-resin.

A second sheet of wax is placed over the missing area.
Air and pour holes have been made in the wax.

Sheet dental wax is shaped to fit inside the vessel and
attached to the glass using a heated spatula.

Polyester clear embedding resin (coloured with
polyester pigments) has been poured between the two wax
sheets and allowed to cure *in situ*. The wax sheets are
then removed.

Cone beaker with trailed decoration, British Museum

Fragments assembled using epoxy-resin.

The rubber mould is re-located behind the missing area, a model of Aloplast is made to represent the glass. More silicone is then used to enclose the Aloplast.

A silicone rubber mould is taken from the interior surface of the vessel.

The Aloplast is removed, the mould replaced and filled with polyester clear embedding resin (coloured with polyester pigments).

CONCLUSION

Although conservation of glass antiquities has advanced in the last decade, the problems of restoration are considerable, not least because the material itself resists strong bonding with adhesives. In addition, the choice of materials is severely restricted due to the need for glasslike clarity and good resistance to discolouration on ageing. Thus there remains the need for continual research into materials with these properties.

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NEW SILICONE RUBBER MOULD-MAKING MATERIALS,
THE ADDITION TYPE SILICONE RUBBERS

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SUMMARY

Condensation type silicone rubbers have been
widely used for mould-making in conservation
for a long time.
Now there is a new family of silicone rub-
bers available on the market, the so-called
addition type silicone rubber.

This paper discusses the advantegeous and
disadvantageous characteristics of the two
types from the point of view of conservation
as well as the different mechanisms taking
place in the vulcanizing processes. It also
describes the problems in connection with
their application in conservation, e.g. the
possible sticking of the condensation type
silicone rubber to the glass-surface origi-
nating from different centuries.
However, using the addition type silicone
rubber on the same glass-surface /i.e. which
the condensation types stuck well/ there is
no such sticking effect. Therefore for the
mould-making of valuable and unique glass
objects the use of the addition type sili-
cone rubber could be suggested.

Silicone rubber mould-making materials vulca-
nizable at room temperature have already been-
used for a long time in order to make moulds
of art objects. Silicone rubbers vulcanizing
by condensation have proved to be good and
become widespread, but for some years now
there has been another type of silicone rub-
ber available on the market in the case of
which vulcanizing takes place by addition.

So far we have not come across any informa-
tion in the special literature or in the
practice of restauration referring to their
being used for the purposes of art objects.
The differences between the two types of
rubber may be traced back to the diverging
mechanism taking place in the course of
curing.

Condensation-type rubbers

Advantages:

Systems of different viscosity to be used in
various forms concerning which experiences
of several decades are available.

Insignificant contraction, adequate dimensio-
nal accuracy.

Disadvantages:

A small amount of /2-5%/ curing catalyst must
be mixed into the relatively great amount of
mixture before use.

Relatively little room for altering the time
of curing by the proportion of the given
catalyst.

The volatile by-products of curing by conden-
sation /e.g. alcohols/ may be harmful.

Addition-type rubbers

Advantages:

The mixing ratio of the two components
/lo:1 - 1:1/ is advantageous because in such
proportions the two components may be mixed
with ease.

By raising temperature the time of curing
may be decreased considerably /to be avoided
in the case of heat-sensitive art objects!!/

During curing harmful, volatile by-products
are not released.

In the course of curing there is almost no
contraction at all, excellent dimensional
accuracy.

Disadvantages:

The catalyst of the system $H_2[PtCl_6]$ may be
inhibited by certain substances.

a/ Silicone rubbers vulcanizing by conden-
   sation at room temperature

The primary component of silicone rubbers
that may be vulcanized through condensation
is dimethyl-polysiloxane containing some
reactive endgroups:

$$HO-Si/CH_3/_2 - \left[O-Si/CH_3/_2 \right]_n -O-Si/CH_3/_2 -OH$$

where n = 5o-1ooo
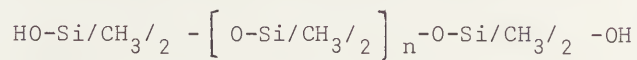
The base material is mixed to form a paste-
like substance of varying viscosity by
adding fillers to it. Before application the
catalyst is mixed into it as well. The cata-
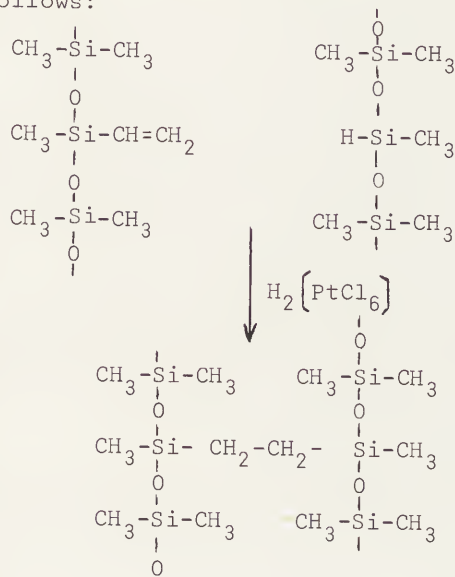lyst contains a vulcanizing compound + some
organo-tin initiator.

In the presence of the simplest vulcanizing
substance, /tetraethoxysilane/ curing may
be described by the following chemical
reaction:
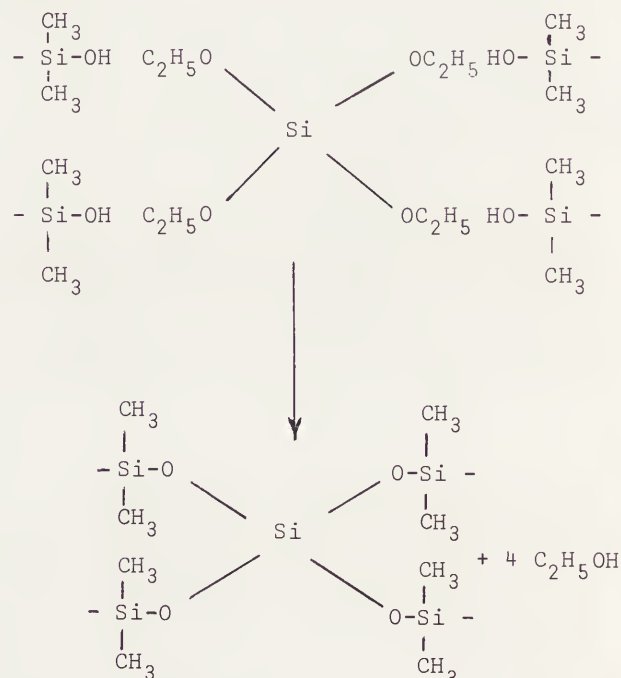
b/ Silicone rubbers vulcanizing by addition

This type is a recent, up-to-date sort of silicone products. They are systems which contain two different components of silicone rubber polymers /methyl-vinyl-polysiloxane and methyl-hydrogen-polisiloxane/.
One of the components /methyl-vinyl-poly-siloxane/ contains a vulcanizing catalyst /most often $H_2[PtCl_6]$/ and both components may contain fillers and additives. After mixing the two components vulcanization will commence slowly at room temperature, though it may be speeded up by raising the latter. In commerce types which cure within 24 hours at room temperature are available.

The process taking place may be described as follows:

$$CH_3-Si-CH_3 \qquad CH_3-Si-CH_3$$
$$|$$
$$O \qquad\qquad O$$
$$|$$
$$CH_3-Si-CH=CH_2 \qquad H-Si-CH_3$$
$$|$$
$$O \qquad\qquad O$$
$$|$$
$$CH_3-Si-CH_3 \qquad CH_3-Si-CH_3$$
$$|$$
$$O \qquad\qquad O$$

$$\downarrow \quad H_2[PtCl_6]$$

$$CH_3-Si-CH_3 \quad CH_3-Si-CH_3$$
$$O \qquad\qquad O$$
$$CH_3-Si-\ CH_2-CH_2-\ Si-CH_3$$
$$O \qquad\qquad O$$
$$CH_3-Si-CH_3 \quad CH_3-Si-CH_3$$
$$O$$

Application for art objects

In the field of the protection of art objects so far the following disadvantageous effects have been reported when applying condensation type silicone rubbers /1,2/. If a separation layer is not inserted during mouldmaking, the silicone rubber may stick to the surface of porous objects /wood, leather, ceramics/. This may be explained by the sucking effect of the surface capillaries, which may be eliminated by the separation layer. In many cases if the application of a separation layer is omitted, even if the silicone rubber does not get stuck onto the surface of the object, the porous material becomes darker and is greasy or oily to the touch after mould-making. Often further difficulties arise by the fact that owing to the porosity of the substance, it is impossible to remove the separation layer completely and the darkening effect may be accounted for by the separation layer itself.

In some cases we found- as it is well-known for condensation-type silicone rubbers - that when making moulds of glass surfaces, the silicone rubber will get stuck to the glass. This effect has been experienced with glasses of varying composition and coming from different ages /e.g. Roman, mediaeval, 19th century glass objects/. It is to be noted, therefore, that there is always such a danger in sight when making moulds of glass surfaces. Often the glass surface is of excellent firmness and is not porous at all /Photo 1./, therefore the process cannot be explained by the rubber impregnating the pores /as it could be claimed for porous ceramic objects/ and may be accounted for exclusively by the similarity in the chemical structure of glass

and silicones.

Photo 1/ Condensation-type silicone rubbers will occasionally get stuck to the glass

The basic material of the condensation-type silicone rubbers may enter into a chemical reaction with the silicic-acidic Si-OH groups to be found in the glass. The presence and amount of reactive Si-OH groups in the glass objects depends on its composition, age, production technology, grade of deterioration and the cleaning process used in conservation. Therefore, it should be pointed out that in the course of making moulds of glass objects, this sticking may probably occur. In each case before starting our work this sticking effect should be tested. The silicone rubber that got set on the glass surface can be removed only mechanically after swelling it in solvents, and in the course of this process the glass object may be damaged or destroyed.

Several brands of condensation-type silicone rubbers were tested on glass surfaces and sticking occured in each case. This led us to try addition-type silicone rubbers with a different system of vulcanizing for the same purpose. This type of silicone rubber did not stick to the surface and could be removed extremely easily /Photo 2./ It seems to us therefore, that using addition-type silicone rubbers, sticking will not occur when applied onto glass and consequently when making moulds of valuable, unique glass objects, addition-type silicone rubbers are recommended. It is advisable, however, to test the addition-type silicone rubber on the surface of the given glass object and estimate the parameters /time, temperature/ of the curing of the rubber in advance.

Photo 2/ Addition-type silicone rubbers are
easily detached from surfaces
which condensation-type rubbers
would get stuck to

Our experiences were gained by using the
addition-type silicone rubbers of Silastic
J RTV and Silastic E RTV of Dow Corning /3/.
The rubbers RTV-ME 622 and RTV-ME 628 of the
Wacker firm are similar /4/.

References:

1. Báthy Géza: Porózus anyagok átmeneti
   felületvédelme. /Temporary surface pro-
   tection of porous materials./
   Muzeumi Mütárgyvédelem 7 /1980/ 7-12.
   Institute of Conservation and Methodology
   of Museums, Budapest 1980.

2. Morgós András: Beszámoló a Szilikon Szim-
   poziumról. /Report on the Silicone Sympo-
   sium./
   Muzeumi Mütárgyvédelem 7 /1980/ 128-134.
   Institute of Conservation and Methodology
   of Museums, Budapest 1980.

3. Dow Corning Europe, Belgium, Chaussée de
   la Hulpe 154. B-1170.
   Silastiv J RTV Silicone Rubber /Bulletin
   61-080/.
   Silastic E RTV Silicone Rubber /Bulletin
   61-183-01/.

4. Wacker Chemie GmbH, Sparte S Postfach
   8000-München 22.

ACRYLIC COLLOIDAL DISPERSIONS AS PRE-CONSOLIDANTS FOR WATERLOGGED ARCHAEOLOGICAL GLASS

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SUMMARY

Primal WS 12, 24, 32, and 50, colloidal dispersions of an acrylic resin, are supplied by Rohm and Haas in a water/alcohol system. The Archaeological Conservation Laboratory, at the National Museum in Copenhagen, Denmark became interested in these products as a possible alternative to freeze-drying, especially in cases where the waterlogged material, such as antler, tusks, or horn, did not respond well to dehydration.

Recently, several fragments of archaeological stained glass were excavated from a waterlogged site. Primal WS 24 in 20% aq. solution was used to consolidate the flaking surfaces. Further examples are discussed.

Primal WS 12,24,32,50[1] are colloidal dispersions of an acrylic resin in a water-based system. According to the manufacturer, the Primal range is similar in composition to and compatible with Paraloid B72.

Koob[2] began experimenting with acrylic colloidal dispersions as a consolidant for fresh archaeological bone. Since the smaller particle size and low viscosity of the colloidal dispersion system permitted better penetration at higher concentrations, he concluded that they were the most suitable consolidant in a water-based system for the consolidation of fragile materials, especially bone and other organic materials because of the near neutral pH. Furthermore, resistance to high temperatures and characteristically good working properties are assured by the Tg, Glass Transition Temperature[3], and MFT, Minimum Film Formation Temperature[4], respectively. In addition, the relatively high moisture barrier, due to an acrylic film's low water permeability and absorption protected an object against climatic fluctuation. After drying, the resin's film was hard, durable,

Before Conservation
Evaporation of water caused severe flaking and cupping of the paint layer and the glass substrate, both on the front and back. (Photo by John Lee)
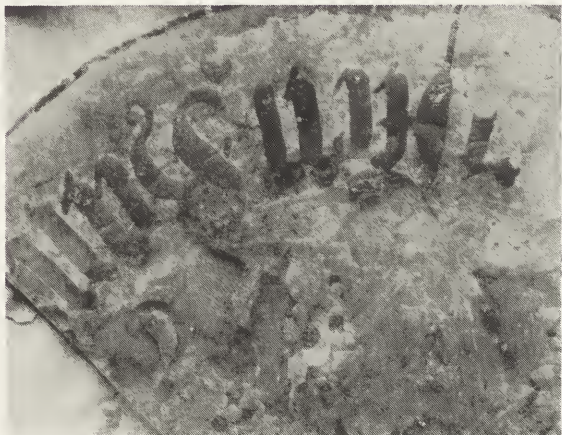
and flexible, as well as reversible in a solvent such as toluene. Accordingly, the Archaeological Conservation Laboratory, at the National Museum in Copenhagen, Denmark became interested in the Primal range as a possible alternative to freeze-drying, especially in cases where the waterlogged material, such as antler, tusks, or horn, did not respond well to dehydration (1).

Several fragments of stained glass, which were in a waterlogged condition were recently excavated. Before the laboratory received the fragments, evaporation of the water had already caused severe flaking and cupping of the paint layer and the glass substrate, both on the front and back. In some areas, the surface was lifting off in relatively thick flakes. Immediate treatment with Paraloid B72, 3% in toluene, was necessary, in order to hold some of the thickest, high-fired paint flakes into position. After observing that moisture relaxed the flaking surface of both the paint and the glass, Primal WS-24 20% aqueous solution was tested on a fragment. Introducing the consolidant at the edge of the glass with a soft brush allowed the consolidant to spread by capillary action. Simultaneously, the moisture and the surface tension of the water drew the very thin flakes toward the glass substrate. As the water slowly evaporated, the Primal WS 24 held the flakes in their correct geometry. In those areas that were previously treated with Paraloid B72, toluene was needed to relax the flakes onto the surface. Surface dirt could then be removed with the combined action of soft sable brushes and slightly dampened swabs. As final consolidation, Paraloid B72, 4% in toluene, was brushed onto the surface.

The same technique was used on a stained glass fragment which had similar problems, but which had not been found under waterlogged conditions. In yet another case, the flaking surfaces were thicker, incorporating both a weathering layer and a thin portion of the glass substrate. Where the Primal technique was not effective, Paraloid B72, 4% in toluene, was used to reattach the flakes, in combination with gentle pressure and slight warmth from a Willard Spatula, type E, and small sand bags.

The Primal technique was especially helpful when consolidating a very fragmented glass bead, dated between the 5th-8th century AD. Unfortunately, the archaeologist had not excavated the bead in situ. It was incautiously placed into a plastic site bag, where condensation moisture added to the bead's already unstable condition. After testing different concentrations of Primal WS 12,24, and 50 under similar moist conditions, using crushed silica gel as glass fragments, Primal WS 24 (100%, as supplied) was chosen as the consolidant and injected through the plastic bag and dropwise onto the surface of the bead. After drying, the combined action of toluene and brushes removed the excess soil. Where the Primal formed an opaque surface, most probably

After Conservation
After treatment with Primal WS 24, 20% aq. solution, the cupping and flaking are reattached to the glass surface. (Photo by John Lee)
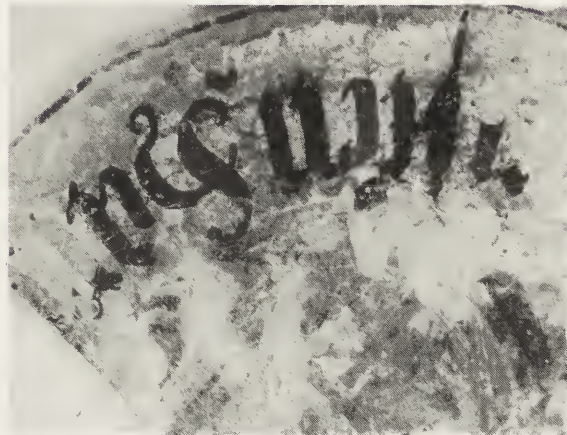
due to drying very slowly under moist conditions,
toluene removed the resin, and an application of
Paraloid B72 reconsolidated the area.

From his investigation, Koob offered a number of
reasons why acrylic colloidal dispersions should
be considered as possible consolidants for organic
materials. In his lecture at AIC-1981 convention
in Philadelphia, he mentioned that Primals could
possibly be used for consolidation of ceramics
in the field. Although further testing should
be done, Primal WS 24 succeeded, at least by
empirical observations, as a pre-consolidant for
waterlogged archaeological glass in the above
mentioned examples.

Footnotes

1.   Primal is the trade name in Europe, while
Acrysol is the trade name in the USA for the Rohm
and Haas, acrylic colloidal dispersion resins.

2.   Stephen P. Koob is the conservator for the
Agora Excavations in Athens, Greece.

3.   The Tg is also referred to as the Second
Order Transition Temperature. Tg lies between
36-39° C for the Primal range.

4.   The MFT lies between 10-18°C for the
Primal range.

References

1.   Koob, S. "Consolidation with Acrylic
Colloidal Dispersions". AIC Preprints 1981,
pp 86-94.

LES JOYAUX DU DAUPHIN, CONSERVATION ET
RESTAURATION (1)

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Instituto de Conservación y Restauración de Obras
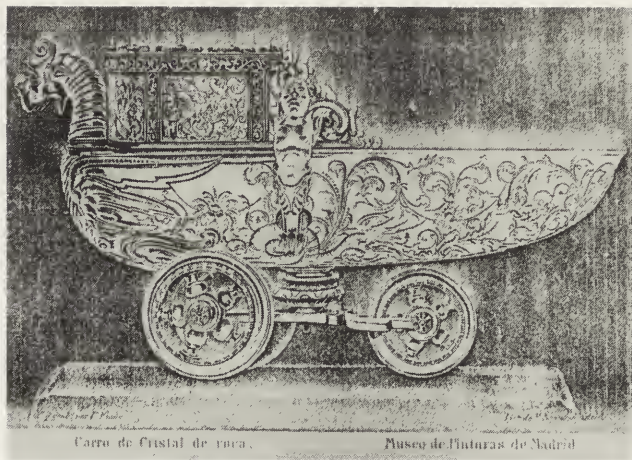de Arte,
Avenida Reyes Católicos, 6, Palacio de América.
Madrid-3,
Espagne

Photo nº 1: Lithographie de Frédéric Kraus vers 1850.
Pièce formant partie de la Collection des Joyaux du
Dauphin, Musée du Prado.

RESUME

La collection des Joyaux du Dauphin qui se trouve au
Musée du Prado est un des échantillons le plus carac-
téristique de la Renaissance et du Barroque. Cette -
collection provient d'un leg de l'héritage de Philippe
V, à la mort de son père, le Grand Dauphin, fils de -
Louis XIV. L'ensemble est formé de 120 pièces de cris
tal de roche taillé et de pierres dures. L'état de =
conservation de cette collection avant sa restauration
pouvait se caractériser par la fragilité et l'insta-
bilité de la plus grande partie de ces pièces, dont -
l'origine se devait en général à des manipulations -
inadéquates pendant les différents transports, le   -
vieillissement des matériaux utilisés l'ors d'une res
tauration antérieure et le vol et la mutilation de =
quelques pièces en 1918. Le critère suivi lors du pro
cessus actuel de restauration s'est basé sur la stric
te conservation des pièces, limitant notre interven-
tion à des méthodes ne pouvant pas abîmer ou modifier
l'intégrité des objets.

1.- INTRODUCTION
Les Joyaux du Dauphin forment une des plus belles co-
llections d'orfévrerie de la Renaissance et de l'âge
Barroque. Ce trésor a également une grande importance
historique pour l'étude et la connaissance des tech-
niques artistiques et industrielles à ces époques. Ils
proviennent de la Maison de France et devaient former
partie d'un ensemble comprenant la collection de cou-
pes en pierres dures ou gemmes, conservée au Musée du
Louvre, et réunie par Louis XIV. Ces pièces avaient
été en général réunies à travers différents héritages
de ses prédécesseurs et une partie fut achetée par
Louis XIV aprés la mort de Mazarin, quand la co-
llection du Premier Ministre fut liquidée. Enfin, -
d'autres pièces furent acquises par la suite pour en-
richir la collection.

A la mort du Grand Dauphin en 1712, et du vivant de
Louis XIV (2), une partie de la collection passa à -
l'héritage de Philippe V. Le 31 Janvier 1724, la co-
llection se trouvait au Palais de La Granja, près de
Segovie, ainsi que les étuis, en général du XVIIIème s.

Le 2 Septembre 1776, Charles III donna l'ordre de les
remettre au Cabinet d'Histoire Naturelle de Madrid. -
Pendant la guerre d'Espagne contre les troupes de Na-
poléon, les Joyaux furent conduits à Paris. Ils res-
tèrent en France jusqu'à la restauration des Bourbons.
En Décembre 1815, ils furent à nouveau conduits en Es-
pagne et installés au Cabinet d'Histoire Naturelle (3).
Quand on recompta les pièces, et face à l'inventaire
de 1776, on constata la disparition de certaines d'en-
tre elles et les dommâges subis par presque toute la
collection (4) (5) (6).

Quand on ouvrit au public le Musée du Prado, son Direc-
teur, José de Madrazo, comprit la valeur artistique de
ces pièces et que celle-ci était supérieure à celle -
des matériaux. Il obtint l'installation des Joyaux en
1839. En 1866, le Directeur du Musée a cette époque,
Frédérique de Madrazo, fit restaurer la collection (7)
qui s'exposa au public de façon définitive dans deux

vitrines héxagonales conçues par l'architecte Juan Ma-
drazo.
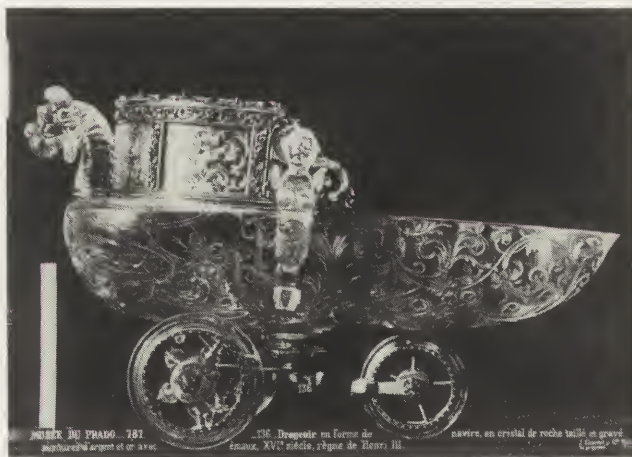
Photo nº 2: Aspect du même bateau. Photographie de
Laurent, milieu du XIXème s.

Au mois de Septembre 1918, on découvrit que onze cou-
pes avaient été volées et que trente cinq au moins -
avaient été mutilées. En 1937, en raison de la guerre
civile, les pièces furent transportées hors du Musée
du Prado où elles revinrent définitivement en 1939.

Les Joyaux du Dauphin se divisent en deux groupes:
celui de pierres dures,agates,jaspes,jades,lapis
taillés,et celui de cristal de roche taillé.Le tout
forme une collection de 120 pièces différentes de
grande valeur.

Les garnitures d'orfévrerie sont en général plus im-
portantes sur les coupes de pierres dures que sur le
cristal de roche.Elles sont en argent,argent doré,
or,bronze,et il y en a quelques unes en laiton.
Quelques coupes de cristal de roche ont une garniture
d'émaux incrustés en général de noir.Les coupes de
pierres dures ont des émaux bleus,rouges,verts et
blancs.Plusieurs pièces ont une décoration de rubis,
d'émeraudes et de diamants.

Les camées sont également importants et on les trouve
dans la décoration de quelques coupes:onix,cornaline
orientale et lapis.Ils sont presque tous de style
renaissance et datent de la deuxième partie du XVIè.s.
et du premier tiers du XVIIème.

2.-METHODOLOGIE ET TRAITEMENT
Nous avons d'abord évalué de manière exhaustive l'en-
semble à conserver et les matériaux qui le composent,

face à leur état de conservation.Les caractéristiques principales étaient les suivantes:mauvaises manipulations subies durant les différents transports,vol des Joyeaux en 1918 ,qui eut,entre autres conséquences,la rupture et la perte de plusieurs pièces,et la restauration antérieure réalisée en grande part avec des
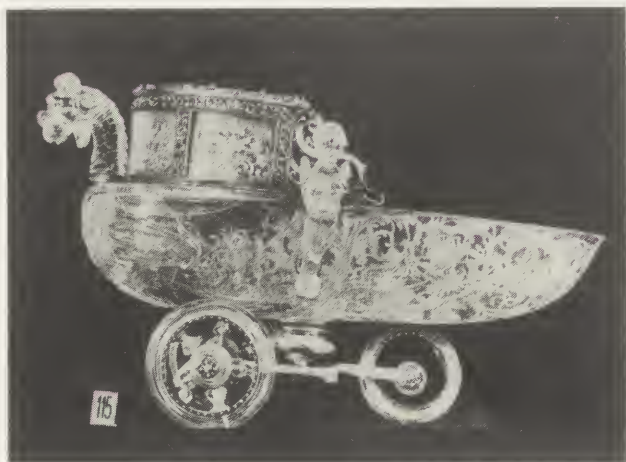

Photo nº 3: Etat dans lequel se trouvait le bateau à la fin du XVIème.s.,avant son traitement.

matériaux organiques(stucs,colles,résines,etc...),qui en vieillissant produisirent la plus part des problèmes de stabilitée des pièces.Les fractures produites sur des zones locales de quelques garnitures furent causées par des soudures à l'étain qui altèrèrent le métal et le rendirent débil.Tout cela, joint à la saletée généralisée,aux sulfurations de l' argent et à la perte partielle ou totale de quelques émaux et à l'attaque de clorures sur les parties internes de cuivre représentait l'état des pièces avant leur restauration actuelle.

Le critère suivit pendant tout le traitement de restauration des Joyaux du Dauphin fut celui d'une stricte conservation,en limitant les interventions à des méthodes qui ne puissent ni endommager,ni affaiblir l'intégritée des objets.Nous n'avons pas considéré la reconstruction de parties manquantes,l'utilisation de soudures et de micro-soudures d'argent.En général,et toujours en tenant compte des caractéristiques particulières de chaque pièce et de son degré d'altération, les traitements suivis furent un nettoyage en surface de façon suave et le retour à la stabilitée perdue.

Pour obtenir ces résultats,nous avons choisi les systèmes les plus adaptés aux caractéristiques des objets ,avec l'emploi de méthodes et de matériaux stables et réversibles.

La méthodologie que nous avons suivi est:
1º.-:Réunion de documentation et de bibliographie.
2º.-:Identification des matériaux en présence dans les objets à conserver. (8).
3º.-:Afin de pouvoir manipuler les pièces pendant leur traitement,nous avons renforcé les cristaux qui présentaient des fissures au moyen d'une gaze qui avait été imprégnée de métacrylate de polyméthyle (Bedacryl 122 X) à 20% en xylène.Cette protection locale initiale fut éliminée par la suite en utilisant du xylène,une fois la pièce restaurée.
4º.-:Selon l'état de conservation des émaux qui décoraient la garniture,nous les avons fixés avec du Bedacryl 122 X dans des proportions variant entre 4% et 8%.
5º.-:Elimination de l'ancienne restauration:Avant d'éliminer les adhésifs vieillis qui produisirent l'instabilitée de la pièce,nous avons pris des échantillons afin de confirmer la composition et la nature de ceux-ci.Pour éliminer les adhésifs, nous avons dû démonter la plus grande part des pièces.Le procédé que nous avons suivi fut celui d'une application locale d'eau chaude desionisée, ou encore l'emploi d'alcohol éthylique,appliqué

au moyen de seringues ou avec du coton.Quand cela s'-avéra nécessaire,nous avons utilisé d'autres méthodes manuelles,comme les burins de joallers et,dans d'autres cas,l'emploi d'un système mixte.

Photo nº 4: Détail du processus de démontage.

6º.-:Nettoyage:
Cristal: Ce nettoyage se réalisa avec de l'eau desionisée,en ajoutant un détergent neutre,non ionique(Lissapol N)à une concentration de 1%, neutralisant le traitement avec de l'eau desionisée.On laissa sécher à l'air les pièces ainsi traitées.Lorsque nous avions une garniture, celle-ci n'était jamais en contact avec l'eau, car nous avons toujours réalisé le traitement de manière locale.Seulement si la garniture pouvait être démontée,nous l'avons retiré complétement et nous avons pu ainsi summerger le cristal dans l'eau de nettoyage.
Pierres dures: Quand nous avions pu démonter les garnitures ou,quand il n'y avait pas de garnitures dans le cas de certaines tasses et de camées,le nettoyage se réalisa par immersion dans de l'eau distilée,en y ajoutant du Lissapol N.Si,au contrai re,il était préférable de ne pas démonter la garniture,lorsque les adhésifs n'étaient pas vieillis nous avons réalisé un nettoyage local avec des tampons de coton imprégnés d'eau désionisée et du détergent déjà cité.Une fois le nettoyage réalisé,ses effets furent neutralisés avec de l'eau désionisée,soit par immersion,soit localement, selon les caractéristiques de chaque pièce.Le séchage fut toujours réalisé à l'air ambiental.
Garnitures :Une fois fixés les émaux au moyen des procédés décrits plus haut,et après une identification qualitative de la composition du métal, nous avons appliqué un nettoyage en surface non énergique ,au moyen de coton imprégné de xylol, dégraissant la pièce par la suite avec de l'acétone et de l'alcohol éthylique.En guise de couche protectrice finale,nous avons appliqué un métacrylate de polymethile(Bedacryl 122 X) à 8% en xylol.
Pour le nettoyage d'un plateau de cristal de roche taillée,qui avait une garniture de laiton, nous avons dû démonter cette garniture afin de corriger les défauts causés par une restauration antérieure et qui présentait une altération de chlorures localisée.Nous avons par la suite employé des moyens mécaniques doux,crayon de fibre de verre,neutralisant les foyers avec de l'oxyde d'argent.Nous avons ensuite séché la garniture dans une étuve à une température de 105º pendant deux heures,appliquant comme protection finale une fine couche de cire microscopique, (Micro S.D. 2.616) dissoute avec du white-spirit.
7º.-:L'union des pièces fragmentées,cristaux,pierres dures et garnitures,fut réalisée avec une résine epoxy(Araldit rapide et Araldit standard) .
8º.-:Nous avons réalisé le remontage des pièces en utilisant des techniques de joallers ou en vissant les différents corps.Quand une partie de la

garniture avait été perdue ou bien se trouvait dans un
état très débile, donc offrant un risque quant à sa
stabilité future, nous avons du appliquer de façon lo-
cale des points de renfort avec la résine époxy déjà
citée.

Pour ce qui est du bateau de la fin du XVIème dont nous
montrons les illustrations photographiques, nous avons
employé des petites barres de métacrylate comme ren-
fort pour les roues afin d'éviter des mouvements brus-
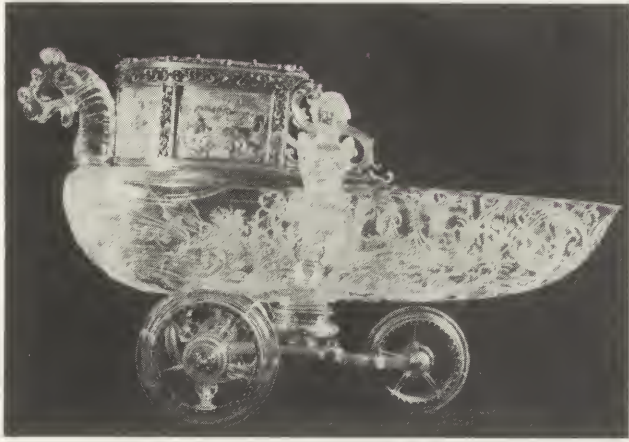ques qui pourraient produire une rupture.

Photo nº 5: Aspect final du bateau, une fois terminée
sa restauration.

9º.- Quand, lors du démontage ou simplement pendant le
nettoyage, nous avons découvert des cachets dissi-
mulés ou des camées taillés sur leur face interne,
nous avons pris des moulures en silicone dentaire
(Coltex) afin de réaliser une reproduction avec
une résine polymerisable en froid de deux compo-
sants (Paladur) afin de la joindre à la documen-
tation de chaque objet.

10º.-Afin d'offrir une protection durant le magasinage
avant l'exposition dans les salles du Musée du
Prado, nous avons enveloppé chaque pièce avec du
papier de soie et des sacs de polyétilène.

11º.-Enfin, un rapport détaillé du travail réalisé a
été rédigé indiquant de façon ample chaque traite-
ment appliqué.

3.- CONCLUSIONS
Nous avons recherché l'élimination de causes d'altéra-
tion des différentes pièces traitées, sans compromettre
l'intégrité du matériel, l'identité documentaire ou ar-
tistique, limitant notre intervention autant que possi-
ble.

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NOTES:
(1) La restauration et conservation des "Joyaux du Dau-
phin" a été réalisée entièrement dans les ateliers du
Musée du Prado de Madrid, où ils se trouvent entrepo-
sés, d'après un projet présenté par l'Institut de Con-
servation d'Oeuvres d'Art. Les travaux ont été dirigés
par l'auteur de ce texte et les collaborateurs suivant
ont participé à la restauration:
Restaurateurs:
    Mme. Carmen Saldaña de Goust
    Mme. Concepción Cirujano Gutiérrez
    Mme. Paz Navarro Pérez
    Mlle. Paz Ruiz Rivero
Analyses:
    Mme. María del Carmen Garrido, Chef du Cabinet de
    Documentation Technique du Musée du Prado.
Documentation Photographique:
    M. Carlos Manso Manso
    Archives Moreno
    Archives Ruiz Vernacci

(2)...à la mort du Dauphin de France, le 18 Février
1712, son fils, le roi d'Espagne, Philippe V, héritat
d'un nombre considérable de joyaux travaillés selon les
goûts les plus exquis du XVIème. Toutes les pièces -
n'étaient peut être pas dues à des artistes italiens
mais plusieurs provenaient des fameux ateliers de Milan,
Florence et Paris. En plus de beaucoup de pièces de -
cristal de roche, entre lesquelles il y a des formes
d'une telle beauté qu'elles ne peuvent être attribuées
qu'à Valerio Vicentino ou aux Misseronis et Sarrahis...
Madrazo, D. Pedro de: "Alhajas del Delfín. Salero de
Onice Oriental". Museo Español de Antigüedades IV,
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(3) Angulo Iñiguez, Diego: "Catálogo de las Alhajas
del Delfín", Museo del Prado. Segunda edición, Madrid
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(4) "....il y avait là les vases précieux de l'école
de Cellini, posés avec précaution, oui, mais mutilés,
leurs anses détachées pour la plus part, les couvercles
cassés, les garnitures bosselées ou déplacées, quelques
uns privés des jolies figures d'émail..." Madrazo, D.
Pedro de (op. cit).

(5) A la fin du siècle dernier, la Maison Laurent pho-
tographia toute la collection, aujourd'hui, archives
Vernacci. Ces photographies, numérotées selon l'inven-
taire de 1776, constituent en réalité un inventaire -
graphique entérieur au vol de 1918. Angulo Iñiguez,
Diego, (op. cit).

(6) Quelques gravures du Litographe du XIXème Federico
Kraus sont également une documentation graphique anté-
rieure au vol de 1918.

(7)"...s'occupa de faire nettoyer et arranger dans le
Musée parce qu'elles étaient susceptibles d'une res-
tauration simple et rapide, sans ajouter ni enlever -
aucune pièce. Cette délicate opération fut réalisée
par le jeune joaller Pedro Zaldos. Restituées en par-
tie à leur brillant d'origine la plus grande part des
riches pièces de l'héritage du Dauphin Louis..." Ma-
drazo, D. Pedro de. (op. cit).

(8) Le système d'analyses employé est celui d'énergie
dispersée de R.X. (Kevex Ray) avec, comme source d'éxi-
tation, l'americio 241. En utilisant cette source, nous
n'avons pas pu identifier les cristaux et les pierres
dures, cependant, nous avons conservé les spectres ob-
tenus. Une analyse de toutes les pièces est prévue par
l'Institut Gemiologique de l'Université de Madrid.

FACTORS AFFECTING THE REFRACTIVE INDEX OF EPOXY RESINS

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Scotland

SUMMARY

In a bid to extend the conservator's ability to adjust the refractive index (RI) of an epoxy resin to a pre-determined value which results in a close match of RI for glass repair, the influence of various factors on the RI of epoxy resin systems has been considered. The RI of an epoxy resin increases during cure till a constant value is reached. This value can be adjusted by the addition of flexibilisers or plasticisers. Dibutyl phthalate and polypropylene glycol both reduce the RI of the cured resin; quantitative results are reported for Ablebond 342-1. The use of alternative hardeners has also been found to result in significant changes in RI for a series of epoxy resins. The effect of the use of alternative hardeners on the photo-stability of the resins has been examined by accelerated light ageing. The changes in RI during ageing of the resins have been found to be minimal, as is the effect of varying the epoxy resin/hardener ratio.

1. INTRODUCTION

The significance of the refractive index (RI) of adhesives used in glass restoration has been investigated recently (1) and it has been shown that when the difference between the RI of adhesive and object is small (i.e. $\leqslant 0.04$), mended breaks and cracks can be almost imperceptible under normal viewing conditions. Since the RI's of historic and artistic glasses span a large range (ca. 1.48 - 1.59) it is necessary that the conservator should have available a wide range of suitable adhesives if a good match in RI is to be achieved. An alternative or supplementary approach is to adjust the RI of commercial adhesives. Since epoxy resins are very widely used as glass adhesives (see, for example, (2)) this paper is devoted to factors which result in variations in the RI of this class of adhesive.

2. EXPERIMENTAL

2.1 RI Measurements

Methods for measuring RI have been described elsewhere by the authors (1). Samples of epoxy resin were cast, ground smooth and lightly polished, prior to measurement of the RI with an Abbé refractometer, using a sodium lamp, and 1-chloronaphthalene for the contact liquid. The Abbé gives greater precision and accuracy than other methods of RI measurement. The accuracy of the instrument was checked against a glass standard of known RI, and the expected error in RI for a given sample is ± 0.0005 (3). Some two-component resins give a greater scatter of values than this, on account of inhomogeneity.

2.2 Accelerated Light Ageing

Ageing was carried out in the Microscal apparatus with an MBTF lamp, as described elsewhere (4,5). The samples for colour measurement were aged inside glass cells until the I.S.O. Blue Wool Standards 4, 6 and 7 showed perceptible fading, and the colour change was examined

at each of these stages. Samples for RI measurement were aged outside the sample cells and were exposed to a higher ultraviolet level. The chromaticity co-ordinates (in terms of the C.I.E.'s 1931 Standard Observer) of the transparent resins over a standard white background were also measured (this procedure is described in (6)), so that the yellowness index (YI) of the resins could be calculated. These measurements are reported in Table 1.

3. FACTORS AFFECTING THE REFRACTIVE INDEX OF EPOXY RESINS

3.1 Factors Beyond the Conservator's Control

3.1.1 Variation of refractive index during cure

The time for full cure of an epoxy varies, and is dependent on several factors, most importantly the ambient temperature. The RI increases during cure, as illustrated by the cure of Ablebond 342-1 shown in Figure 1. In this case, a constant final value of 1.5646 was reached after 3 days. The plot of RI versus time is not smooth; the dip in the curve after ca. 10 hours may correspond to the gel point, though this feature was not observed by Dannenberg (7) in a paper which proposed the determination of RI as a method for monitoring the cure of epoxy resins. Obviously it is the final value of the RI which is relevant for glass repair. It follows that the appearance of a resin-filled crack should improve as the epoxy cures.
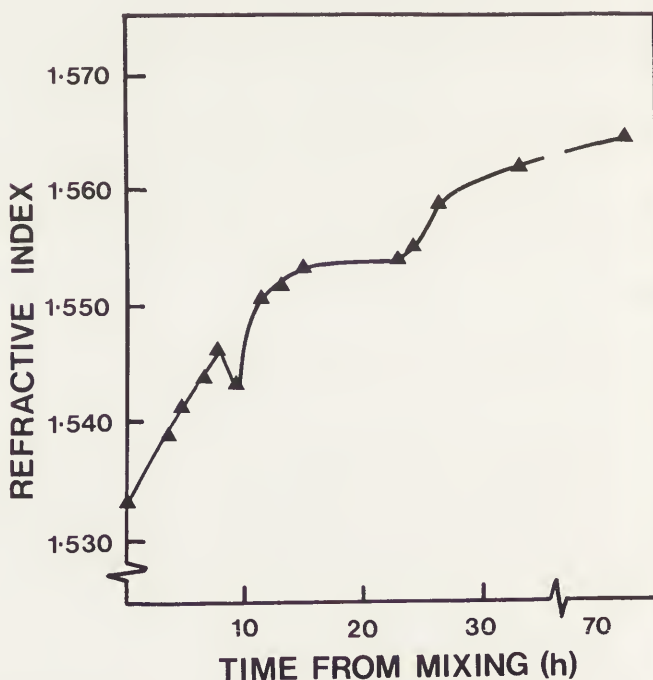

Figure 1. Variation of refractive index during the cure of Ablebond 342-1.

3.1.2 Changes due to ageing of the resin

Epoxy resins are susceptible both to photochemical (4) and thermal (8) degradation. For museum display, glass is generally subjected to strong illumination, so it is important that the RI of epoxy adhesives should remain stable as the resins age. It has been shown that, for narrow cracks, a close match in RI between the adhesive and glass is more important for achieving an invisible repair than water-white clarity of the resin (1).

The RI of a series of epoxy resin/hardener combinations was measured before and after accelerated light ageing at a slightly elevated temperature (45°C), and the resulting differences in RI are shown in Table 1. The yellowing of another set of these samples is also reported in the Table and it can be seen that, despite the less severe ageing conditions for these samples,

Table 1 Change in yellowness index (YI) and refractive index (RI) of various epoxy resin/hardener combinations after accelerated light ageing (Microscal MBTL lamp)

RESIN SYSTEM (Base/Hardener Names)	INITIAL YI (t=0)	ΔYI (t=53h)	ΔYI (t=144h)	(t=580h)	INITIAL RI (t=0)	ΔRI (t=360h)	(t=792h)
HXTAL NYL-1 (own hardener)	2.5	(a)	(a)	(a)	1.5201	(a)	-0.002
Ablebond 342-1 (own hardener)	2.1	1.7	3.8	7.2	1.5646	+0.004	+0.004
Ablebond 342-1/HXTAL NYL-1	6.3	22.5	45.9	68.8	1.5737	(a)	-0.002
Ablebond 342-1/Araldite HY951	7.3	23.0	34.5	47.1	1.5887	(a)	-0.002
Araldite AY103*/HY951	5.8	16.6	28.0	41.3	1.5740	+0.002	+0.004
Araldite AY103✿/HY951	7.6	19.7	28.7	39.5	1.5784	(a)	+0.003
Araldite AY103 /Ablebond 342-1	2.3	7.2	12.6	14.3	1.5523	+0.002	+0.002
Araldite AY103 /Ablebond 342-1	2.2	4.2	8.4	11.2	1.5600	(a)	-0.004
Araldite AY105/HY951	7.1	15.8	24.7	33.5	1.5850	+0.003	+0.001
Araldite AY105/Ablebond 342-1	2.1	1.7	4.0	6.6	1.5675	-0.001	-0.001

(a) ΔYI and ΔRI are less than or equal to the experimental error

* Upper fraction from container containing AY103 resin

✿ Lower, more crystalline, fraction from container containing AY103 resin
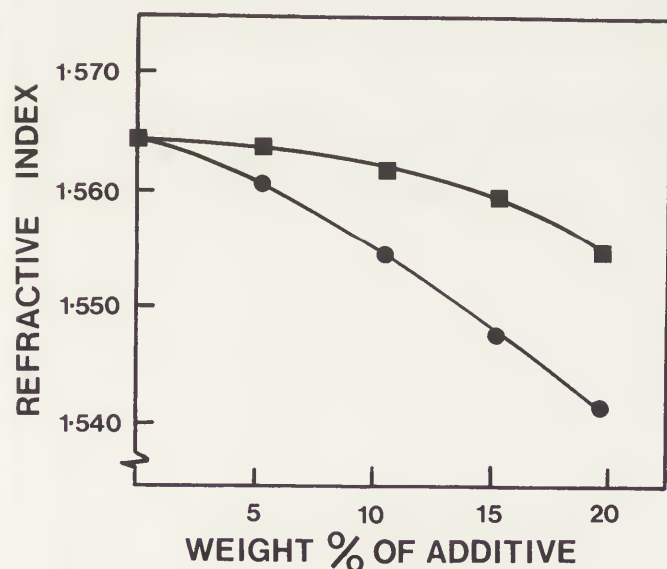
Figure 2. Variations in the refractive index of Ablebond 342-1 due to the addition of Araldite DY040 flexibiliser (●) or DBP plasticiser (■)

the change in yellowness is much more pronounced than the change in RI. The yellowing is quoted in terms of the yellowness index (YI); a change in YI (ΔYI) of 2 or 3 is just perceptible when comparison with an unaged specimen is possible. A water-white resin undergoing a change in YI of about 10 would be just perceptibly yellow under normal viewing conditions. A study of the Table shows that the largest change in RI was 0.004, and that increases and decreases both occurred. The direction and size of these small changes are not obviously related to resin composition. For the purpose of matching the RI of adhesives and objects in restoration, the change in RI as these resins age is negligible.

3.1.3 Batch-to-batch variations

These tend to be small for epoxy resins, and rarely exceed ± 0.002. Commercial resins which do not contain additives and which are fairly free of impurities, or resins intended for casting or mounting specimens for microscopical examination, show even smaller batch-to-batch variations.

3.2 Methods of Varying the RI of Commercial Epoxy Resins

3.2.1 Addition of flexibilisers and plasticisers

Modifying the properties of an epoxy resin with additives such as flexibilisers or plasticisers provides a chemically sound means of altering the RI of the cured resin. A series of Ablebond 342-1 casts was made up with 0-20% additions (i.e. weight of additives/ total weight of all components) of Araldite DY040, a polypropylene glycol flexibiliser, or dibutyl phthalate (DBP) plasticiser. The RI of the casts is shown in Figure 2. The addition of 20% by weight of Araldite DY040 caused the RI to drop by nearly 0.025 from the normal value, while DBP caused a smaller drop of 0.01. Either additive is therefore useful for modifying the RI of the cured resin over a small range, but while Araldite DY040 does not appear to affect the yellowing of the resin, DBP has been shown to enhance it (4). The effect on the strength of bonded glass is likely to be minimal.

3.2.2 Varying the proportion of base to hardener

The appropriate mixing proportions for epoxy resins can be calculated for any epoxy resin/hardener combination on the basis of the epoxy equivalent of the resin (9). For optimal properties, it is important that the correct proportions be maintained by weighing the components accurately. It is therefore not a good practice to modify the RI deliberately by varying the resin/hardener ratio. In a bid to determine what the effect on the RI would be, several casts of Ablebond 342-1 were made with a 25-30% excess or deficiency of hardener. Their RI was found to vary by ± 0.003 from the usual value of 1.5646; too small a variation to be useful for adjusting the RI for glass repair. The addition of dyestuffs to colour resins for gap-filling also results in insignificant RI changes.

3.2.3 Use of a hardener other than the recommended one

Several epoxy systems used in glass restoration are similar chemically, in particular those based on a diglycidyl ether of bisphenol A with an amine hardener. This includes Ablebond 342-1 and the Araldite AY103 and AY105 systems. It is possible to interchange their

hardeners and produce a different cured resin. The strength of the cured resin could be adversely affected, but many conservation applications do not require the full adhesive strength of epoxy resins, so that the advantage of modifying the RI outweighs this disadvantage.

The RI's of Ablebond 342-1, Araldite AY103 and AY105, and HXTAL NYL-1 epoxies with their own or another hardener,are shown in Table 1. HXTAL NYL-1 resin, a 2-aminopropyl ether derivative of a triol, was also investigated. The resins with their own hardeners have the following RI's: 1.520 (HXTAL NYL-1), 1.565 (Ablebond 342-1), 1.578 (Araldite AY103/HY951) and 1.585 (Araldite AY105/HY951). Interchanging them produced new values between 1.552 and 1.589, a range which is useful for the repair of certain objects (1). Not all the base-hardener combinations have been attempted here, but trends can be seen for the behaviour of a given hardener in different bases. For example, the hardener Araldite HY951 confers a high RI on the cured resin. (The lower RI of Araldite AY103/HY951 compared to AY105/HY951 is a result of the presence of dibutyl phthalate in the former system).

The properties of the resins are likely to be modified if a hardener other than the recommended one is used. Only one property, the tendency to yellow on ageing, was examined. The mixed resins underwent accelerated light ageing and their colour before and after ageing was compared, by the use of the yellowness index (see Section 2.2). Table 1 shows that some combinations had an improved light stability over the standard components, while others yellowed more. It was pointed out earlier that the yellowness of the resin in a narrow crack does not affect the appearance of a repair, but the resistance to yellowing of untested resin/hardener combinations is not always good enough for casting missing areas.

4. CONCLUSIONS

The practical difficulties of producing an epoxy resin system with a specified refractive index have been discussed. The systems considered here (Ablebond 342-1, HXTAL NYL-1, Araldite AY103 and AY105) are sufficiently reproducible that the conservator need not worry about batch-to-batch variations or alterations in the RI after natural ageing. When necessary it is possible to adjust the RI slightly by the addition of compatible flexibilisers or plasticisers, or, if a more drastic modification is required, by combining different (but compatible)resins and hardeners. Accelerated light ageing tests underline the necessity of testing new resin/hardener combinations prior to use in situations where yellowing of the polymer would be a disadvantage.

SUPPLIERS OF MATERIALS

Ablebond 342-1; HXTAL NYL-1: Conservation Materials Ltd., 340 Freeport Blvd., Sparks, Nevada 89431, USA.

Araldite AY103, AY105, HY951: Ciba-Geigy Plastics and Additives Co., Plastics Division, Duxford, Cambridge, CB2 4QA, UK

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Section 21

Training in Conservation and Restoration

Formation en conservation et restauration

HIGH LEVEL, BASIC LEVEL AND MIDDLE LEVEL TRAINING IN CONSERVATION. WHAT DOES IT MEAN ?

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Summary – The author argues that anybody responsible for preservation or conservation of historic and artistic works must at least have a basic knowledge of conservation. Art historians or natural scientists who do basic research for conservation should have a thorough understanding of conservation problems. This does not have to include the training and skills of operating on the object. Those actually working on such objects, the conservator/restorer or those consulting in conservation, the conservation scientist must have a high level training in conservation.

The topic I choose has been irritating me for some time. I always added question marks and never quite understood when – often in a very unpresice manner – the notions – high level, basic level and middle level training in conservation – were used. To use unprecise notions when discussing training in conservation does not help, but adds to the slight fog that still seems to be hanging on the subject.
The fog I am refering to hinders the definition of what is needed to assure an appropriate conservation of cultural heritage and a precise definition of the professional activities concerned.
This fog is not of course on the minds of conservation specialists but – and that is important – it often is around people who by their position and responsibility have influence and authority to decide on the right or wrong development in conservation and training in conservation. It is therefore important that we should agree on certain basic requirements and understandings of our profession and state them accordingly as guidelines and information for others.

When generally looking into problems of education and training it is essential to look for what is needed. When looking at our particular problem – training in conservation – we realize that a number of different professionals are and will be concerned with conservation and that they all must be trained. These are architects, engineers, town planners, historians, art historians, ethnologists and archeologists, craftsmen in conservation, natural-scientists and conservator/restorers.
Except for the conservator/restorer these professionals are normally trained without regard to their possible later activity in conservation. They receive – on different academic levels – a training as architects, historians, craftsmen etc. Their training as such is not a point for discussion except of course where their knowledge about conservation problems is concerned.

It is different for the conservator/restorer. In most countries his activity is not an officially recognized profession and the professional designation "conservator/restorer"is not legally protected. As this working group has pointed out before: "anyone who conserves and restores is called a conservator or restorer, rather than those, who have been trained properly". There is no recognized standard or level of training, his status is controversial and goes from zero to recognized authority in his field, mostly dependent of his training.

It is to be recognized that a considerable effort is made all over the world to preserve mankind's cultural heritage, but it must be admitted that this effort is insufficient and often far from appropriate. The question of what is needed to advance conservation efforts should be answered as follows: more awareness about conservation problems generally, more in depth knowledge about the significance of objects and the relationship between form and matter, more thorough professional education, training and qualification for anybody directly concerned with conservation ! The question of who is needed with what training in conservation could – according to my understanding – be answered as follows: Curators, archeologists and technical museum staff should at least have a basic knowledge about conservation and its problems and – particularly for the curator and the archeologist – a thorough understanding of objects as material realities and direct sources of documentary information.
Natural scientists, art historians and ethnologists should have a full understanding of conservation problems. As it is their role to contribute with high level basic research on the materials, technology and conservation of objects their "training in conservation" should obviously be comprehensive.
Architects, conservator/restorers and conservation scientists are needed with a high level knowledge about conservation and in conservation to directly work in that field either consulting or – as a physician – on the object. Their knowledge and understanding of conservation problems must be comprehensive, including historic, esthetic and material contexts as well as the training and skill to work on the object. They must be educated in that "research attitude" that will identify all the object-related contexts first, analyze their relevance and only then decide if and how to interfere on the object.
Well trained craftsmen or technicians trained in a craft for maintenance, renovation and reconstruction, particularly in monument conservation, are needed as a last mentioned – but by no means least important – category of professionals in conservation. Their training will be on a technical level but should include the teaching of historic technics of the crafts, good knowledge of material and an understanding of the significance of the documentary value of historic substance. It must also include a basic understanding of conservation problems. This category of professionals should be directed in their work by people with a more comprehensive training in conservation. But it is utopian to believe that anybody can be directed to do a good job who does not understand what it is all about !
It is – by the way – also utopian to have these people "directed" by somebody with high level academic training but with no training in conservation himself ! I particularly mention this because in some museums, archives, libraries and excavation sites

this is still considered acceptable.

Considering the evolution in our profession
during thatlast two decades and considering
the basic rule we have recognized in our
definition of the profession, namely that
any conservation or restoration problem
should only be approached by first methodi-
cally taking into consideration all aspects
involved, there is no doubt in my mind that
anybody directly concerned with conservation
- either as a consultant or actually working
on the objects - must have a training in
conservation on the highest level. This
level must have an academic status such that
systematic approach of problems is taught
as thorougly as theoretic knowledge and high
level manual skill.
High level training in conservation must not
be confused with an academic degree in histo-
ry of art or in a natural science. The trai-
ning there does normally not include any
consideration of conservation problems.
High level training in conservation should
become a required and normal academic career
for anybody - conservation scientists, con-
servator/restorer, architect - who intends
to embrace a responsibility in conservation.
It should in consequence become equally nor-
mal that anybody who does not have this
training may not call himself a conservator/
restorer or take upon himself the responsibi-
lity for conservation or restoration work.
Basic training about conservation problems
should be required for anybody who has an
administrative responsibility in the museum
field or in monument conservation.
It should also be required from anybody who
- in whatever quality - works under somebody
elses supervision on objects of historic or
artistic significance.

THE TRAINING OF RESTORERS AT THE MUSEUM FÜR DEUTSCHE GESCHICHTE AND ITS RESULTS AND EXPERIENCES

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SUMMARY

Since the 1976 academic year restorers have, in a four-year technical school study course, been trained in the following specialities: restoration of prehistorical cultural assets and those stemming from early history, of musical instruments, for archeological excavations, of books and papers, metal, wood, textiles as well as of ceramics and glass. Since the course started 65 extra-mural students have successfully completed the course as well as 16 students who have done so by correspondence. An additional 17 students are due to complete their studies this year.

The course is conducted by the department of training and further training at the Museum für Deutsche Geschichte. Basic training is provided centrally while matters specific to the various subjects are handled at different consultation centres generally situated in restoration workshops in possession of the necessary facilities.

The course is conducted entirely on an extra-mural basis and the students continus to work in restoration workshops during their studies. This ensures close links to the practical side of things in the training process. The academic and theoretical level of the lectures and other events is therefore a demanding one. Themes for the final papers are chosen in close collaboration with the institutions in which the students are employed. As a result most of the papers are of a high academic level. In addition most of them are of such a nature and quality that they are of practical use in restoration work.

The experiences gathered in running this course are being used continuously to improve the entire training process. An extension of the course through the introduction of two further specialities - leather and stones - is being considered.

Systematic training of restorers has taken place in the German Democratic Republic since 1968 and diplomas have been awarded for this profession for the last 15 years by the College of Fine Arts (Hochschule für Bildende Künste) at Dresden. A decisive stap in the academic training of restorers was taken with the introduction of courses at college level. However, by virtue of the fact that training concentrated mainly on restorers for paintings and wooden sculptures the problems facing particularly the GDR's museums were not solved yet.

The range of tasks facing restorers is considerably wider and cannot be coped with only by those qualified in restoring paintings and sculptures. All spheres of restoration work with which museums are faced require qualified members of this profession. It was for this reason that an additional opportunity for training had to be provided which takes into account the full width and great variety of creative restoration work.

In 1975 the Museum für Deutsche Geschichte was entrusted with this responsibility and as a result a department of training and further training was set up. Starting with the 1976/1977 academic year, a course at technical school level for the training of restorers in 8 specialities saw the light of day. We are now training personnel in the following specialities: restoration of prehistorical cultural assets and those stemming from early history, restoration of musical instruments, restoration - archeological excavations, restoration of books and cultural assets made of paper, metal, wood, textiles and finally ceramics and glass. By going in for these eight avenues of specialization we believe that we have catered for the most important spheres of restoration work required by museums. At the same time - and based on the need to preserve historical monuments - the Potsdam branch of the technical school for commercial art (Fachschule für Werbung und Gestaltung) started a course for architectural restorers.

By training restorers in these specialized directions we think that we have filled a gap and as a result the GDR is now training professionally qualified restorers for all types of museums at college or technical school level. These new directions taken in training restorers are due to the constantly increasing demands on the quality of his (or her) work and the social and scientific responsibility of the restorer in our museums operating as they do in a socialist environment. He (the restorer) after all also has his part to play in seeing to it that our people achieve a healthy relationship to their cultural heritage. The original objects of the material and spiritual culture of the people and its environment are being preserved and cultivated as witnesses of the past, as a means of comprehending the present better and of making the future more active. As a result the demand that science should increasingly penetrate the sphere of restoration and the call for scientifically trained for restorers was therefore in line with objective necessity.

The introduction of a course of this kind in 1976, ranging as it does over a wide spectrum, was not easy. True enough we were able to fall back upon a range of experience as courses for restorers had been run for many years at the Museum für Ur- und Frühgeschichte Thüringens in Weimar, at the Landesmuseum für Vorgeschichte in Halle, at the Musikinstrumentenmuseum at the Karl Marx University in Leipzig, at the Deutsche Bücherei and at other institutions. Nevertheless the majority of our restorers as a rule acquired their knowledge and skills largely in the course of practical work. It was directly during the course of work with and on various objects that they gathered their experience, exchanged them and widened their vision and in all essentials continued to train themselves autodidactically. There was no systematic and standardized training encompassing the entire range of restoration work in a purposeful and scientific manner.

This left its special mark on the technical school set up at the Museum für Deutsche Geschichte. Within a relatively short span of time all scientific facilities were provided

for this discipline and all its specialized fields. At the same time it was necessary to ensure the provision of the educational and organizational preconditions for a course of study in such width. The most important aspect of this was the provision of a standardized, centrally guided training course while at the same time making sure that this would be as close to actual practice as possible. At the same time it was necessary to make use of already existing resources and to do so fully. The course is therefore organized in such a manner that the department of training and further training at the Museum für Deutsche Geschichte provides the central management while consulting centres have been set up at a number of museums which have at their disposal restoration workshops suitable for this purpose. Centres of this kind exist at the Museum für Ur- und Frühgeschichte Thüringens at Weimar, the Musikinstrumentenmuseum at the Karl Marx University in Leipzig, at the Landesmuseum in Halle, at the Deutsche Bücherei in Leipzig, at the Museum für Deutsche Geschichte as well as at the Staatliche Museen in Berlin. In addition practical training is also carried on at other technical schools, excurtions are arranged to specific workshops and specific parts of the training syllabus are completed at other institutions, e.g. the restoration of drawings at the Kupferstichkabinett (print room) of the Staatliche Kunstsammlungen in Dresden.

All eight specialities are taught on the basis of binding curricula. These on the one hand contain studies basic to all specialities such as the social sciences, German, Russian, the theory of culture, aestethics, the history of art and museology and on the other subjects relevant to practical work such as a knowledge of materials, methods of research based on the natural sciences, chemistry of relevance to the profession, technology of conservation and restoration, documentation/photography etc. The major part of the basic studies takes place during the first year of study and the share of profession-related study increases year by year. The last year of this 4-year extra-mural course is largely used to prepare and write the final examination and its practical part.

A special problem both in designing and later carrying through this course of study consisted of the fact - and still does - to ensure under all circumstances not only that the future graduate is capable of carrying out a wide range of work but that he can, at the same time, dispose of basic knowledge and specific skills in his speciality. Thus the subjects are identical in most specialities and the wood restorer, just as his counter-part in metal, glass and ceramics, is not only instructed in the knowledge of materials, subject-related chemistry, the technology of conserving and restoring etc., but the concrete conveying of this knowledge is closely linked to the specific discipline. Thus all these subjects are identical for all specialities but their contents differ in terms of the specialization. Naturally there are also subjects related to the individual specialities.

All eight specialities are taken as an extra-mural course and no other form of study was found to be possible in view of the fact that there was an accumulated demand for trained people in this profession and in as wide a range as indicated above. In the meantime practical experience has shown that this type of course, in addition to having a number of disadvantages, also has numerous advantages in its favour. The student is already working and is also working in a restoration workshop during the course and can therefore carry out practical exercises during his working day. On the other hand the participant in the course already has, in most cases, several years' experience when commencing his studies. He therefore does not need to acquire the skills of a tradesman and is already acquainted with most materials. The studies can therefore concentrate on deepening this knowledge and these skills and capabilities. And, and this is the most important aspect, the academic and theoretical level of the course is therefore a high one. At the same time the continued activity of the student in his profession together with his specialist studies, ensures that the entire study course is practice-related. However, this form of study presupposes that the applicant must, prior to commencing his studies, already have had practical experience of some length of work in a restoration workshop. As a rule therefore, a typical applicant will be older than his counter-part applying for a course of full-time study.

No new institutes were established following the launching of the course because the individual consultation centres happen to be restoration workshops of long standing and are particularly suitable for the various avenues of specialization. In addition to academic staff in the various discipline, restorers of proven ability are active as lecturers. Practical exercises are carried out on the spot and this also applies to the completion of special exercises in the laboratories. There are close links with other educational establishments and with enterprises of various kinds and these are utilized in the organization of excursions.

Independent study, as is known, is the chief method used in extra-mural courses. When this new course commenced - no text books or synopsis was available - the necessary materials for independent study had to be made available at the same time as the curriculum was drawn up and these have been steadily improved over the years. In addition to study guides of a high quality, detailed material is now available in a number of subjects and in some cases textbooks are already available.

The eight years which have passed since the introduction of the course were years of garthering experience and of proving ourselves and for testing in practice our academic groundwork because it was a characteristic of the course that not very much experience was available in this sphere. Thus in principle something new had to be created: not only the academic groundwork had to be carried out for a course of this kind but it had to prove itself in practice. We were of course able to gather new experiences immediately training and practical work commenced. These are constantly assessed, processed scientifically and in turn applied in the training process. As a result both the curriculum and the teaching programmes and study materials have been amended in the light of practical experience. Thus the curriculum is now available in its third edition and we are now working on a still newer version.

Even though we are in a position to assert that a good basis and good preconditions have been created for this course the whole thing continues to be a process for us, something in fact on which we are continuing to work in order to improve its quality and effectiveness. We are already considering whether the eight specialities are adequate and

whether some extension is required, for ex-
ample in respect of restoring leather or
stones. However, now as before our major
consideration remains the further deepening
of the scientific and theoretical content of
the course. In the meantime we have been
able to obtain the services of a number of
additional academics and their work as lec-
turers in this study course as well as their
full-time jobs in scientific institutes -
where reasearch also takes place - provides
us with the starting point of tackling some
as yet unsolved scientific problems in the
interests of training and with that in the
final analysis raising the quality of res-
toration work further. Let me but mention
the restoration of glass or the conservation
and reinforcing of old wooden items.

Since the course came into being 65 extra-
mural students have passed their examin-
ations and 16 candidates have completed
their technical school course by correspon-
dence. The end of the present academic year
will be witness to 17 additional candidates
passing their final examinations. By the
middle of this year 100 qualified restorers
will be employed in the GDR's museums. At
present a total of 71 students are under-
going training in our course and in addition
there are an additional 15 participants
sitting in at lectures or at only some of
them.

Our technical school course for restorers is
still relatively new but in the meantime we
have at our disposal not only a fund of ex-
perience but can also look back upon re-
sults which can indeed be cause for satis-
faction. The students' final papers are
without exception of high academic quality
and of much practical use. The subjects are
chosen in close cooperation with the insti-
tutions in which the students work. This
results in the fact that the majority of
the papers are such that they are of immedi-
ate use in future restoration work.

At a session of the Working Group Training
in Conservation and Restoration held in
Dresden in September 1983 we gave viewers an
idea of the details and results of our
course with the help of a small exhibition.

EDUCATION IN CONSERVATION OF MUSEUM PROFESSIONALS IN POLAND

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ABSTRACT

The greater practical demands imposed on museums staff members the essential collaboration with restores, scientist and technician. The process of conservation is essentially those of partnership between curators and conservators. The paper deals with teaching of princip les of conservation in regular academic studies of archaeology, etnography and art history in M.Curie Skłodowska University in Lublin. The aim of rule lectures and seminars is to enable future curators, assistant curators and members of staff of service for monuments care to communicate meaningfully with colleagues specializing in other disciplines concerning conservation.
Post graduate and in service training in the requirements of conservation available to curators is recently organised in Poland.
The increasingly demands imposed on curators the essential collaboration in conservation and there is a need to raise the training of curators in conservation on higher level.

EDUCATION IN CONSERVATION OF MUSEUM PROFESSIONALS IN POLAND.

The conservation of our curtural heritage is developing in Poland on several ways on the basis of the government's cultural policies, creation of the service for monument s care and interest of people in optimal maintenance of monuments and antiquities.
There are an organised system for training professional restores in Poland, mainly in painting, sculpture, graphic in the Academics of Fine Arts in Warsaw and Cracow as well as in Fine Arts Department of the Nicolai Copernic University at Toruń. We have also some secondary and high schools of arts and crafts teaching restoration of exhibits textiles, metals and wood. Some informal basis for training of restores exist in restoration workshops of museums and of State Enterprise for Monuments Conservation where the training is realised in the way of interships.
The reports on the training of restorers-conservators at Academics of Fine Arts in Poland have been elaborated by Prof. Mieczysław Stawicki/Academy of Fine Arts Warsaw/ and Prof. Władysław Slesiński/Academy of Fine Arts Cracow/ and the report on the intership of conservation students by Dr. Janusz Lehman/National Museum in Poznań/ and exposed at the Meeting of TCR-Working Group in Dresde 5-9 September 1983. My interest as lecturer at M.Curie Skłodowska University in Lublin is in teaching principles of conservation future museums curators and assistant curators as well as members of staff for State Service of Monuments Protection. State Enterprise for Monuments Conservation and for other institutions of antiquities and monuments care. Museum staff members are educated in the way of regular studies at Universities in courses of history of art, history, etnography and archaeology. The main subjects studied are theoretical and specialised in mentioned above social sciences. Apart from the entrance qualifications and examination students must have the neccesary scientific and proffessional inclination which are examined over entire studies and during compulsory practical work experiences at a suitable museum or monument care institution. The study programm covers a learning period of five years and humanistic disciplines are supplemented by basis lectures in museology, monument's care and fundamental methods in conservation. The main purpose of supplementary studies in museology and in conservation consists in the mediation of humanistic preparation to museum's actvities related to the cooperation with conservators restorers, scientists and technicians in work progress. The interest of museum besides scientific and educational work relies upon well being of collections lead to preoccupation with preservation. The museum staff is expected increasingly to perform a role as a guard specialised to monitor all museums functions - also preservation in close collaboration with a specialist conservator. Museum curators need help and advice from conservator and restorers about many problems as storage, especially of the more delicate exhibits, proper display in showcases and lighting, safeguard and protection, control of museum's climate general maintenance and cleaning of exhibits, packing and transportation, handling of exhibits for temporary or travelling exhibitions. In the aim to prepare students for the future work in museum the programm of studies in archaeology, etnography, the history and of art at M. Curie Skłodowska University in Lublin provides lectures and seminars as well as training in museology and conservation of museum s objects. The object of the training is general knowledge about conservation, handling, storage of exhibits, museum s climate, materials, techniques of works of art and crafts. According to our pedagogical conception, training of history of art is an humanistic study but it is generally appreciated that some scientific knowledge on materials, techniques and conservation of works of art is now a necessary component of any archaeolog s historian of art training course. The academically educated historian of art working in museum should generally:
- understand the decay mechanizm of antiquities and works of art and how to counteract damage,
- be familiar with determination and measuring of climate and lighting conditions,
- know conservation and restoration methods of antiquities and works of art which are concern of him

- be able to evaluate the functional value of
  conservational and preventional measures,
- be able to prepare all types of documenta-
  tion for antiquities and works of art inc-
  luding photographic and description of pe-
  rformed treatments,
- understand materials and technology of an-
  tiquities and works of art which are con-
  cern of him.

In recent years the Association of Art Histo-
rian in Poland, the bigger museums in Poland,
State Officies for Monuments Conservation and
State Enterprise for Monuments Conservation
and State Enterprise for Monuments Conservat-
ion have had many discussion to discover what
is ideally needed for an efficient system for
teaching historian of art, etnographs and ar-
chaeologs in principles of conservation and
every day maintenance of museum's collections
and exhibits as well as to elaborate a unified
system for training conservators and restorers.
At the international level it appeared recent-
ly two very important documents after the Mee-
ting of ICOM Commitee for Conservation.
Working Group Training in Conservation in Dre-
sde 5 - 9 September 1983, namely:
a/ The Conservator-Restorer, a definition of
   the Proffession
b/ Recommendation to international and natio-
   nal associations about recognition of tra-
   ining on basic principles of conservation
   as idispensable for art historican, archi-
   tects, archaeologs, etnographs, librarians.

It is to emphasize that since some tenths of
years great attention has been given to the
scientific background of conservation and to
the technical training of conservators-resto-
rers and very little has been discussed about
the role of the curator in the processes of
conservation. The curator requires also an
appriopriate training to undertake that role.
The process of conserving collection or sole-
ly object is necessarily the product of a pa-
rtnership between conservators and curators,
and thus it is essential that both are able
to communicate meaningfully with colleagues
specializing in the other discipline.
Many responsible conservators and curators wo-
uld not challenge there principles but their
application is well high impossible under exi-
sting level of training and education both,
conservators and curators. The amount of lectu-
res and seminars on principles of conservation
during regular studies of history of art,
archaeology, etnography at the M.Curie Skłodow-
ska University in Lublin as well as in all Po-
lish Universities is far insufficient. The in-
service training in the requirements of conser-
vation currently available to senior curators
remains almost non-existent. Courses of stu-
dies in principle of conservation organised on
international level are frequented mostly by
conservators-restorers. At national level du-
ring recent years many attention has been gi-
ven to the in-service post graduate studies in
museology at Jagielloński University in Cracow
and in conservation of monuments and sites at
Technical University-Department of Architecture
in Warsaw. These studies are primarily concer-
ned mainly theoretically with the historical and
aesetical aspects of problems and introduce

very little of scientific and technical prin-
ciples of conservation. Anyway the begining
of progress of studies in very wanted direct-
ion has been made. These demands are of cru-
cial importance for future developpment of
conservation services since by their nature
highly trained and experienced curatorial staff
actually or potentially will be able to fulfil
their role in conservation. The specific res-
ponsibility of curator in the conservation is to
to extend initial examination and subsequent
treatment and to approach any objects from
background of practical experience to an al-
moust entirely theoretical view-point.
It is increasingly important to realize the
partnership between curators and conservators
in the processes of conservation.
It is to emphasize that this partnership shall
rely on a day to day basis, or even on an hour
to hour basis and it presupposes the existence
of curatorial staff in close proximity to the
conservation workshop with adequate time at
disposal to fulfil this function.
That day to day basis for partnership is poss-
ible in the national and major provincional
museums and art galleries. Conservation servi-
ce of small museums and art galleries staffed
by relatively low experienced curatorial staff
with operate without curatorial advice under the
potentially hazardous conditions or it will
have to employ experienced curators from major
museums or it will have to be closely asso-
ciated with the national or district museum in
order to get on a day to day advice and exper-
tise required. Some auxuliary role fulfil con-
servation conferences organized on national
and international level.
The member of curators attending such conferen-
ces is relatively small and the emphazis on
technical papers is understandably of real va-
lue to a minority of already technically-orien-
tated curators and conservators restorers.
The conservation has a tendency of constant de-
velopment, that can be used to maintain a high
level of work and interest. New means of prov-
iding studies and in service training must be
created for both curators and conservators.
In this mission the ICOM - Commitee for Con-
servation, and in particural Working Group
Training in Conservation and Restoration has
to fulfil its essential function.

EDUCATION IN CONSERVATION: THE NATIONAL GALLERY OF CANADA

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SUMMARY

Conservators at the National Gallery of Canada play a
role in educating others concerning conservation-related
matters. Advice, consultation and training extend to
National Gallery Staff, and beyond, to the conservation
profession and other museum professionals. In addition,
publications, lectures and exhibitions are directed at
the general public. Artists are provided with advice
regarding the stability of their materials and methods.
Architects and consultants are informed of the conserva-
tion requirements of the New National Gallery of Canada
Building.   * * * * * * * * *

The most obvious responsibilities of the conservators at
the National Gallery of Canada, Ottawa, involve caring
for the collections through an active program of
preventive conservation, conservation treatment and
research. There is, however, another very important
aspect of our conservation activities: that is,
Educating others with respect to conservation-related
matters. This activity includes the informing and
advising of several groups of people within the National
Gallery of Canada (NGC): curators and administrators,
education staff and installations personnel, workshop
preparators, framers and security guards. This
educational function extends outside of the NGC to other
conservators, museum professionals, artists and the
general public.

1. NATIONAL GALLERY OF CANADA STAFF

Conservators advise NGC Staff on such matters as general
care and handling, display, photography, storage and
transportation of works of art, as well as the important
requirement of environmental control. Installations
personnel are kept informed of standards for light levels,
and materials safe for use in case design. These
activities have the aim of ensuring a high standard of
care for the NGC collections. Periodic Custody Workshops
involving all NGC Staff help to reinforce good custodial
practices and serve to inform all departments of the
responsibilities of other departments within the NGC,
along with procedures to be followed. The principle of
"shared responsibility" for the works of art in the care
of the NGC is promoted.

It is the responsibility of the conservator to provide
the curator with information concerning the materials
and techniques of the artist (which may affect the art
historical interpretation or value), the causes of
deterioration or damage of works of art, the range of
methods and materials which can be used in conservation
examination and treatment, and the implications of any
treatment proposed. The type of damage which can be
incurred during exhibition or loan, and the means by
which this can be prevented or at least minimized, must
be explained by the conservator, so that the full
implications of travelling and exhibiting works of art
are appreciated by the curator.

During 1983, the Conservation Department, together with
representatives of the Curatorial and Exhibitions
Departments, developed an NGC Conservation Policy. As a
result, the role of the Conservation Department has been
more well-defined, along with specific conservation
responsibilities of the NGC. Authority and decision-
making with respect to the conservator and the curator

are set out in the Policy and Procedures. Preparation
of the Conservation Policy was an educational
experience for all involved, as all policy and proce-
dures were reviewed and evaluated. This document is
now being used to inform all staff of NGC conservation
priorities and procedures.

2. CONSERVATION PROFESSION

The conservators at the NGC play an important role in
preparing lectures and publications directed at the
conservation profession. Participation in local,
national and international conferences encourages the
dissemination of information concerning NGC conserva-
tion activities: research projects, examinations and
treatments carried out. We are called upon to give
occasional lectures to students in the Queen's
University Conservation Training Program. The NGC
Conservation Department has also initiated and
organized two major conservation conferences: Lining:
A Reassessment (1976) and the International Symposium
on the Conservation of Contemporary Art (1980).

One of our most important educational functions,
however, is the training of conservation interns. The
NGC provides internships of three to twelve month
duration for graduate students in recognized conserva-
tion training programs in Canada and elsewhere.
Internships may also be arranged for conservators with
other previous practical experience. All conservators
at the NGC become involved in training of the interns,
attempting to provide a challenging, stimulating and
valuable experience for the trainee. The Conservation
Department must organize internships to correspond with
space and staff limitations. Interaction of the
interns with the NGC curators and other staff is
encouraged, to give the intern a sense of the concerns
and complexities of work in a major museum. Interns
are not relegated to menial tasks, but their internship
time is viewed as an opportunity for invaluable "hands
on" practice under careful supervision.

3. OTHER MUSEUM PROFESSIONALS

The NGC recognizes the fact that other museums and art
galleries throughout the country look to it for leader-
ship and guidance in many museological matters,
including conservation. Standards set by the NGC- for
environmental controls (temperature, RH, lighting,
atmospheric pollutants), care and handling of works of
art- have been strived for at the NGC, and have been
provided as guidelines for other institutions for many
years. These guidelines and requirements are
disseminated by the NGC Department of National Programs
(responsible for coordinating travelling exhibitions of
NGC works throughout Canada), and are set out in NGC
Loan Agreements (under Responsibilities of the Borrower).
These recommendations are in keeping with those of the
Canadian Conservation Institute.
By educating other institutions about how to better care
for their collections, that is, through emphasizing
preventive conservation measures, the NGC is helping to
ensure generally improved standards throughout the
country. Results of this are immediately obvious in
applications made to National Museums of Canada funding
programs such as the Museum Assistance Programs :
Canadian museums are applying for grants to upgrade
their environmental conditions and lighting systems,
often so that they can become eligible to receive
exhibitions organized by the NGC.

The Canadian Conservation Institute in Ottawa is
extremely active in the area of education of museum
personnel through their Mobile Laboratory programs,
Care of Collections slide kits, Technical Notes and
Technical Bulletins. However, the NGC assumes the
responsibility of further educating museum professionals
who will be dealing with borrowed NGC works.

Museum professionals visiting the NGC often tour the
Conservation Department. We provide explanations of the
role of the department, and demonstrate some of the
conservation treatments which are in progress.

Lectures and seminars have been provided in the past by
the NGC conservators, directed toward museum profes-
sionals other than conservators. I feel that an even

greater emphasis should be placed on this area, in order to communicate to other museum curators, directors and Boards of Directors, the importance of conservation and its place in their museums. This should help to ensure that conservation activities and precautions will be adequately supported and funded. Workshops have been held at the NGC for client galleries- stressing connoisseurship, techniques of the artist, recognition of signs of deterioration, as well as preservation of works of art.

NGC conservators have been called upon to participate in task forces and advisory boards when input concerning conservation activities and responsibilities is required. At such times, our standards and practices are communicated to individuals or organisations making decisions and developing policy which will affect the preservation of cultural property.

4. GENERAL PUBLIC

The Conservation Department of the NGC provides an educational and information service to the Canadian public. We respond to personal, written and telephone enquiries concerning the care of works of art, causes of damage and deterioration, as well as to queries with respect to conservation and restoration. Brochures and other publications on the care of works of art are provided to the public free-of-charge.

Monthly clinics are conducted in which private individuals may bring, by appointment, works of art to the Conservation Department for examination and technical information. Identification of signs of deterioration, explanation of the importance of preventive conservation, and discussion of the ethics and philosophy of conservation are provided. In addition, previous and possible future restoration are discussed. These clinics are held in co-operation with the curators who will first provide information on attribution or provenance. Criteria for selection of a qualified conservator are provided. Referrals can be made to competent conservators when required. Clients are referred to external organisations for appraisals or valuations of their works of art. Occasional special clinics have been held in the past in which NGC framing and conservation staff have advised the public concerning safe framing practices.

Occasional tours of the Conservation Department are arranged for university and college student groups, for example, through the Department of Education. An annual NGC Open House draws hundreds of visitors to the scheduled tours of the Conservation laboratories.

The NGC Conservation Department organized the exhibition Progress in Conservation (1972), in which an attempt was made to demonstrate the interaction of conservation, the physical sciences and art history in examining and preserving works of art.

The NGC Conservation Department also participated in the Know What You See Exhibition organized by Louis Pomerantz for the Foundation of the American Institute for Conservation, and circulated by the Smithsonian Institution in 1979. Examples of NGC works, which had been examined in the Conservation Laboratory, were added to this exhibition when it was displayed at the NGC.

NGC conservators give occasional external lectures or full-day seminars to the public on the care of collections, technical aspects of works of art, or conservation examination and treatment. We take part in the NGC "Gallery Talks" coordinated by the Department of Education; general audiences are addressed by a conservator on a conservation-related topic.

NGC conservators are approached from time to time by the media for radio, television or newspaper interviews on conservation matters. These opportunities provide a means to educate the public concerning various aspects of the conservation field. NGC conservators have also been called in to provide examination and testimony in Art Fraud court cases in Canada.

Discussions with respect to the New National Gallery of Canada, which is currently under construction in Ottawa, have included proposals for a Conservation Didactic Area to explain examination and treatment recently completed, or to demonstrate various principles of conservation.

5. ARTISTS

The NGC Conservation Department receives, more and more frequently, enquiries from artists who are concerned about the compatibility, stability and permanence of materials and techniques which they are using. Some useful information can be provided, but much research must be done in this area before we will be able to answer, with confidence, many of these technique-related questions.

By initiating a dialogue between the conservator and artist, each party will learn and benefit from the other. Such was the partial aim of the NGC International Symposium on the Conservation of Contemporary Art (1980).

We try to encourage artists to document the materials and methods they use in their creations. The NGC has initiated a new Questionnaire for Artists, with the aim of collecting this information, in addition to the artist's intention in terms of permanence, deterioration and future conservation or restoration treatment. In this way, the artist is educated about the concerns of the conservator.

6. ARCHITECTS AND CONSULTANTS FOR THE NEW NGC

Information concerning conservation requirements for the NGC collections is communicated to architects and consultants who are responsible for the designing and construction of the New National Gallery of Canada. Input of the Conservation Department is essential to ensure that the decision-makers understand the importance of, and give due consideration to, environmental controls, movement of works of art, storage and display requirements, throughout the planning process.

CONCLUSION

The aim of the above-mentioned educational or informational activities is to promote a greater understanding and appreciation of the techniques of the artist, the causes of deterioration of works of art, and methods of preventing damage and degradation through proper care and handling. The conservator describes the techniques used in the scientific examination and treatment of works of art, and trains interns in the museum environment.

An important result of these educational activities is the generation of a greater awareness, in many sectors, of what conservation is and what the conservator does. Education of this kind will help to further the aim of preserving our cultural heritage.

LE SERVICE SOCIAL DES ETUDIANTS DE RESTAURATION AU MEXIQUE

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54740, Edo. de Mexico, Mexico

Resumé - Depuis que la carriere professionelle de restauration du patrimoine culturel a été crée, l'application d'un aspect de la loi des professions au Mexique a été nécessaire. Cette loi comprend l'accomplissement d'un service social, qui fait partie des conditions, que l'étudiant doit remplir à la fin de ses étude pour la présentation de son examen professionnel. C'était dans les ateliers du Centre de Restauration que les premiers élèves ont rendu ce service en accomplissant ainsi les conditions légales, mais sans remplir les intentions idealistes qu'a formulé la loi: de faire un travail utile à la communauté qui puisse servir surtout au groupe sociale qui a le plus besoin d'information relative à la specialité. Durant les dernières années, on a pu rendre ce service, suivant l'esprit de la loi, et le resultat fût, à part qu'il était avantageux pour un groupe défini, une meilleur compréhension des élèves participants du but réel de leur carrière: "La conservation du patrimoine culturel de l'homme, laissant de côté les intérêts mesquins leur propre comodité, ou leur bénéfice économique. Ce service est fait pendant la periode de vacances, alors le resultat est avantageux pour la formation des élèves, leur éveillant le sens de la responsabilité et de service.

L'année 1910 connaît un mouvement armé au Mexique. Ce mouvement est connu sous le nom de "La Révolution Mexicaine"; même si au départ il ne surgit que comme un mouvement politique avec la seule finalité d'enlever le pouvoir au général Porfirio Díaz qui s'était perpetué dans la presidence pour plus de trente ans. Le mécontentement des ouvriers dans les villes, des paysans journaliers dans les "haciendas" et d'un petit groupe d'intelectuels, ont donné au mouvement un sens et une orientation différents à ceux qui l'avaient originé. Vers 1916 le Congrès constituant se réunit pour élaborer une nouvelle Constitution Politique qui substituera celle de 1847: le gouvernement de Venustiano Carranza organise les élections pour nommer le Congrès Constituant et le 21 Novembre tient lieu la première session dans laquelle on aprouve les cartes des députés; le Congres s'installe le premier décembre à la ville de Queretaro. Deux mois plus tard, le 31 janvier 1917 la nouvelle Constitution fut terminée et promulguée le 5 février de la même année. La réprésentation dans la chambre des différents groupes qui étaient en lutte, a eu comme résultat une Constitution d'un vaste contenu social. Par exemple, la loi agraire qui a exproprié la terre labourable des "haciendas" et l'a remise entre les mains des paysans, ou la loi de la Sécurité Sociale qui garantit aux travailleurs et à leur famille des soins médicaux (maternité, médicaments, crenche, crêche, allocation vieillesse etc).

L'article trois de la Constitution Mexicaine dit: "L'éducation donnée par l'état féderal, états, municipalités, tendra à developer harmonieusement toutes les facultés de l'être humain et encouragera chez lui l'amour de la patrie et la conscience de solidarité internationale, de l'indépendence et de la justice...//...le critère qui orientera cette éducation se maintiendra totalement étranger à une quelconque doctrine réligieuse et basé sur les résultats du progrès scientifique...//...contribuera à améliorer la conscience humaine...//...la conviction de l'interêt général de la société quant au zèle qu'elle mette à soutenir les idéales de fraternité et d'égalité de droits de tous les hommes...//...Toute l'éducation que l'Etat donne, sera gratuite...//...le Congres de l'Union, afin d'unifier et coordonner l'éducation partout dans la République, expédira des lois destinées à distribuer la fonction sociale-éducative parmi la fédération, les états et les municipalités..." De cet article trois constitutionel, émanent les lois d'éducation et des professions, dans lesquelles on conserve ce sens social que marque la Constitution. Ces lois imposent comme retribution du diplomé la compensation en heures-homme au profit de la société, cherchant avec cela un travail utile à la communauté et sur tout utile à la partie de la société qui a le plus besoin de la spécialité de l'enseignant.

Dés la création des études de "conservation et restauration de biens culturels", le besoin d'accomplir cet aspect de la loi sur les professions s'est fait sentir comme un impératif pour avoir le droit de présenter l'examen professionnel.

Pour toutes les études de sciences, en plus de la thèse professionnelle, on exige de l'élève d'avoir un minimum de six cents crédits académiques et dans le cas d'études qui récquièrent une pratique manuelle, les heures d'atélier forment le cinquante pour cent du quantum formé par les matières théoriques et le service social de 1500 heures de pratique dans l'exercice de la profession; dans ce cas il existe aussi des systèmes pour valoriser le temps de travail, dépendant des conditions sous lesquelles a lieu ce service:
a) Dans la ville de Mexico et sa périphérie une heure de travail effectif est comptée comme une heure de service social.
b) Dans les capitales des Etats et les villes importantes de la province, une heure de travail effectif compte comme deux heures de service social.
c) Dans les zones rurales, une heure de travail effectif est considérée comme trois heures de service social.
d) Dans quelques zones spéciales on a compté comme quatre heures et même d'avantage, selon le manque de facilités et services, communication, commodité etc. que chaque lieu présente.
Les premiers élèves qui réalisèrent cette mission, l'ont fait dans les atéliers mêmes du Centre de Restauracion; remplissant ainsi la demande légale, mais sans satisfaire la fonction réelle que l'esprit de la loi a implicité; qui n'est rien d'autre que celui mentionné plus haut: l'aide à la communauté qui a le plus besoindu dit bénéfice social. L'accomplissement pur et simple de la demande légale, ne comble pas l'objectif final des études: former du personel pour recupé-

rer et conserver le patrimoine culturel de
l'homme. Car en créant dans la conscience
de l'apprenti l'esprit de service envers sa
communauté, on lui crée une conscience
d'accomplissement de la demande légale de
n'importe quelle façon; seulement pour sau-
ver la démarche légale qui prend l'aspect
d'un poid mort d'une affaire totalement
bureaucratique sans importance et qui ne
fait que retarder le bénéfice inmediat
que l'on obtient grace à un diplome pro-
fessionel; comme par exemple, commencer
à gagner de l'argent, la comodité passant
avant la finalité de la conservation du
patrimoine culturel.
Ayant soufffèrent l'expérience des premiers
groupes, les autorités scolaires ont senti
le besoin de réorienter le service sociale
en changeant les lieux dans lequels le ser-
vice se réalisait pour d'autres qui réunis-
sent les caractéristiques adéquates pour
aider à la formation éthique du futur pro-
fessionel.
Pour faciliter l'accomplissement du service,
l'Ecole a organisé le travail pour les
périodes de vacances scolaires nommant des
"conseillers du service" professeurs en
temps complet. C'est à dire ils travaillent
huit heures par jour pour l'Ecole, faisant
cours et orientant les élèves dans les
problèmes techniques ou académiques. Pour
cette fonction ont été nommédes élèves
ayant terminé leurs études et qui volon-
tairement se sont offerts pour profiter de
cette expérience de travail et pour en faire
leur these professionnelle basée sur la
solution d'un problème réel. Avec l'avantage
que l'orientation qu'eurent les premières
theses vers le domaine de la recherche
humaniste, a été changée par thèse avec
des problèmes de conservation de pieces et
qui, pour la première fois, englobèrent
les trois aspects des études: l'humanisme,
la science, et la technologie.
Le travail dans la plupart des cas, s'est
présenté comme travail de groupe et de façon
multidisciplinaire. C'est à dire, tous les
étudiants pouvaient opiner, proposer, diffé-
rer ou suggérer sur le travail à réaliser
et le conseiller modérait et orientait. Dans
le cas où le groupe ne se mettait pas
d'accord ou bien décidait un chemin équivoque
le conseiller pouvait, avec toute l'auto-
rite que lui donne l'Ecole, décider du type
de traitement et l'imposer au groupe.
Avec l'aide d'une psycologiste spécialiste
de l'éducation, les étudiants se sont pré-
parés pour travailler avec la communauté et
de l'y associer en la faisant participer
aux travaux, colaborant dans des petites
tâches ou dans des missions spéciales, comme
des travaux de charpenterie, de forgerie ou
de maçonnerie. Pour ce faire, on engageait
des ouvriers de la localité et on invitait
les autres habitants de payer ces frais et
de loger et nourir les restaurateurs. Aux
élèves on a désigné des tâches en accord
avec leur degré d'avancement et compétences
naturelles. Quand le besoin s'est fait sen-
tir on a demandé à l'Ecole le secours de
spécialistes: chimistes, biologistes, des-
sinateurs spécialisés dans un domaine spé-
cifique ou bien des historiens, archéologues,
architectes ou muséographes.
Pendant les dernières années de la décennie
des soixante dix, on a pu prêter ce service
tel que le prevoit la loi et le résultat,
outre celui déjà prévu du service à la
comunauté qui en a le plus besoin, a été
la prise de conscience des élèves partici-
pants de la finalité réelle de leurs études:
La Conservation du Patrimoine Culturel de
l'Homme; laissant de côté les intérets mes-
quins comme la commodité personnelle, le
bénéfice économique inmédiat etc. Ceci a pu
être valorisé quand les élèves ont présenté
leur feuille de service pour présenter
l'examen professionel, non pas avec les mil
cinq cents heures que demande la loi, mais
avec mil huit cents, mil neuf cents, deux
mil et même plus de deux mil cinq cents
heures.
Comme le service social se fait pendant les
vacances scolaires l'expérience a bénéficié
les élèves dans leur formation, les faisant
plus responsables et enthousiasts dans les
heures de cours et d'atelier. Il y a eu des
élèves qui sont retournés au lieu de leur
service les jours de fêtes ou les fins de
semaine pour terminer un détail qui n'avait
pas été fini, ou pour s'assurer que le
traitement choisi avait été adéquat et que
rien de mal arrivait à la pièce restaurée.
Mais, sans doute, la valorisation exacte
des bénéfices obtenus avec le changement, se
trouve dans le developpement professionel
des élèves qui ont terminé leurs études et
qui vécurent cette expérience. Comparés avec
le developpement professionel de ceux qui
ont fait le service avec les caractéristiques
précedentes, ceux-ci pour la plupart, n'ont
pas voulu travailler pour l'état car ils
considèrent infime les salaires qu'on leur
offrait et ont travaillé pour des particu-
liers, pour des universités, faisant cours
d'histoire de l'art et d'autres dans des
dépendences de l'éducation comme chercheurs
d'art. Les autres, au contraire, ont lutté
pour obtenir des meilleurs salaires exerçant
leur profession, les uns comme employés
du gouvernement, les autres dans les insti-
tutions éclésiastiques et le reste travaillant
comme particulier. Mais touts luttant pour
les idéales qu'ils se sont formés pendant
leur préparation: vivre de l'exercice de
leur profession sans trahir cet objectif
final de leurs études: "Conserver le Patri-
moine Culturel de l'Homme".

RESEARCH AND DEVELOPMENT AS AN INTEGRAL PART OF TEACHING

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SUMMARY

Training centres are also centres of research and development. The involvement of students for the restoration of art treasures in research work is an integral part of training and done in cooperation with scientists and art historians.

A description is given of the principles of research in conjunction with teaching, and the specificity and special features of research efforts with restorer students.

Teaching and research

Teaching is unthinkable without the systematic advancement of working methods and the extension of knowledge by research work. Training centres are, therefore, always centres of research and development. This hardly disputable statement, however, does not say anything about the character of research work to be done by restorers, and which rank and which extent is to be attributed to teaching in general.

We hold the view that academic training of restorers should not be understood as a higher-ranking workshop training. A certified restorer has to learn scientific working methods, analyse experience, collaborate with art historians and natural scientists and has to work scientifically without any assistance. This does not mean that a restorer also shares the job, or would be able to do the job, of a scientist and art historian.

Principles of research in teaching

- Enabling the students to work with scientific literature;

- Teaching the capacity to abstract things and draw analogous conclusions;

- Enabling future restorers to realise the objects and problems at work in their environment, i.e. perceiving things in a larger scientific interrelation;

- Training the preparation of scientific work programmes, the systematic implementation thereof and an exact documentation in writing and in pictures;

- Arousing the understanding of the inter-disciplinary nature of modern conservation and restoration efforts by profound familiarisation with a clearly defined field awaiting exploration, and qualification for requisite cooperation;

- Distributing different subjects within a study group. Providing the possibility of learning from neighbours. Public defence or presentation of results. Most fruitful should be the discussions in which colleagues of all disciplines should participate;

- Involving research in teaching at a time when a student feels disburdened from course works, consultations and examinations. This is a time at which a student has the mental concentration and maturity to be scientifically creative, with the enrichment of artistic creativeness having been well familiar to him/her since long;

- Consistent limitation to problem-oriented research (possible and necessary for undergraduates to a limited extent).

Integrating research in teaching

A prerequisite for the integration of research and developmental problems in teaching may be:

- well-trained teaching staff who are conversant with the principles of research and development work and who have gained extensive experience in this sphere;

- well-equipped and -furnished rooms creating the precondition for scientific work;

- the maintenance of cooperative relations to specialised institutions in special fields;

- well-functioning and continuous assessment of the current international literature, a publication service of one's own and a regular exchange of experience on an internationa scale;

- the involvement of research in studies at a time when basic knowledge and basic skills have been conveyed in order to have practical research and development tasks settled as part of the curriculum;

- adequate monetary support

Cooperation with natural scientists

Every restorer has to have such a scientific knowledge that he/she can estimate the behaviour and applicability of materials for conservation and restoration, make experiments and blend the materials with each other, and he/she is acquainted with important test procedures and potentialities. Only that way becomes he/she the partner for collaborative research efforts with scientists. Special emphasis should be laid on the term "partner", for all test procedures and analyses are usually made by a natural scientist himself and not by a restorer. Hence, a restorer should exactly know his/her professional limits.

Moreover, only the restorer is in a position to derive the direction of the research work from his/her practical work on the object under restoration. The array of well-proven working methods and materials does not suffice to cope with all impacts a work of art is exposed to. Known shortcomings in the methods applied and materials urge to search for new solutions. Research themes often derive from the restorative tasks to be tackled on the object.

Even basic research is bound to themes or subjects which have to be primarily developed for the restorer. This means that research work on the restoration of art treasures is unthinkable without the partnership of restorer and scientist.

Student receive partial tasks for themes in the following fields:

- constant testing of materials that may be found suitable for conservation and restoration;

- development of new working methods and techniques for the application of new materials;

- perfection of the technological potentialities and test procedures to investigate causes of damage and for analyses of the condition of objects under restoration;

- advancement of special methods such as glueing methods for relining (hot seal glue, adhesive glue), low-pressure techniques, welding of fissures, wood impregnation methods etc. according to the specialised field.

Cooperation with art historians

The restorer's knowledge of arts should be such that he/she is able to roughly classify the objects under restoration with regard to time and place. He/she has to be made acquainted with the art historian's research methods to such an extent that he/she can fulfil partial tasks of art-historical research efforts with his/her specific means (studies of painting techniques, evaluation of radiographic diagnoses), thus becoming an indispensable partner of art-historical research ventures in museums and the institutions for the preservation of historic monuments.

During training, our undergraduates are familiarised with the methods of comparative analyses of stylistic elements, painting habits and the critical assessment of radiographs and infra-red pictures. They get object-related partial tasks for seminar work or in the diploma year that promise new findings when the restorer's methods are applied:

This applies to such tasks as:
- classification of a picture by painting techniques (time and place);
- comparative studies of underpaints;
- workshop habits in the handling and choice of the painted panel or the carved material;
- coverage of facts on the history of a work of art (pigments, scratches, pretreatment of the painted ground etc.).

It is also essential that undergraduates be trained in handling technical literature.

We are of the opinion that a qualified restorer may not only be a higher-ranking craftsman but that he/she can do scientifically founded work as an academically educated specialist without sacrificing artistic and dexterous faculties.

If the involvement of all undergraduates in research efforts is emphasised this way, we conclude that training centres bear a great responsibility for the trial and general publication of working methods. In any case the educational level of graduates reflects the level of academic training. The quality of the work done and the choice of working methods for the preservation of art treasures in a particular country and also beyond it depends largely upon the level of training.

CONSERVATION: UNIVERSITY STUDY OR EQUIVALENT?
TWO TRAINING MODELS

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SUMMARY

Two different training systems for conserva-
tors/restorers have recently been proposed in
Norway. Both aim at the highest level for aca-
demic education in the country (Ph.D. or equi-
valent degree). One model proposes the inte-
gration of conservation into the existing uni-
versity subjects, while the other recommends
an independant school to be established.
The discussion of the two alternatives raises
a question that may not be entirely trivial:
do we want curators with a formal competence
to restore, or restorers with a formal cura-
torial competence?

Introduction

Last year, a committee appointed by the Royal
Ministry of Culture and Scientific Affairs sub-
mitted a report on conservation in Norway,(1)
comprising proposals for revised training sy-
stems for conservation personnel. Our prelimi-
nary considerations have already been reported
to this working group.(2) A discussion of our
final recommendations will be given in the
following.

To some extent, the differences in restorers'
training systems throughout the world are due
to the different ways national education is
organized in the various countries. A brief
description of the structure of higher educa-
tion in Norway is therefore given below before
describing the two models.

Practically all museums and all conservation
activity in Norway are parts of the official
economy (state or municipal). Therefore, a
formalization of educational criteria, with
reference to other professions involved in
museum work - particularly curators - was a
perspective that our committee could not avoid.
For this reason, the presentation in the fol-
lowing is more concerned with the formal frame-
work, and less with the actual contents of the
study.

"Scientific High Schools"

The "High School" concept in Scandinavia is
similar to that of the German "Hochschule",
and is generally applicable to any school with
"gymnasium/baccalauréat" (12 years) as a pre-
requisite. There are about 170 institutions of
this kind in Norway.

"Scientific High Schools" is a concept restric-
ted to those schools conducting research. We
have got 6 institutions of this category: the
High Schools for Commerce, Agriculture, Sports,
Architecture, Music, and the Art Academy.

"Scientific High Schools" rank equally with
the universities, and their teaching staffs
are granted the same titles, formal status and
salaries as university professors and lecturers.
Some former schools of this kind, such as the
High School for Technology, have in fact been
absorbed by one of our universities for mere
organizational reasons. These institutions re-
present the highest attainable levels within
their respective fields.

Although allowing considerable freedom for re-
search, the 4- to 7-years' courses given by
these schools are scheduled as independent,
closed systems within their own framework.
University exams, for example, are normally
not credited and cannot substitute parts of
their curriculum.

Universities

With the exception of certain "closed" facul-
ties, like medicine and law, our 4 universities
as a rule offer possibilities for a vast number
of flexible combinations. Exams can be taken in
a wide range of subjects after one-, two, three-
or four-semesters' courses, and combined to
form a base for a Ph.D.- or equivalent degree.
This base combination must correspond to 4
formal years (8 formal semesters) of study.

A complete doctoral study in Art History, for
example, may be planned as shown in Figure 1,
next page.

In recent years, the flexibility of this system
has been extended. Combinations are now possible
with subjects also from outside the universi-

Base study: 8 semesters (4 formal years)   Ph.D. or equivalent work*)

| 1 sem. | 2 sems. | 3 sems. | 2 sems. | 2 - 3 years |

Philosophy,   French   Art history   Archaeology   Art history project
compulsory   literature
introd.   *) "Magister" and "Doctor" degree systems presently under revision
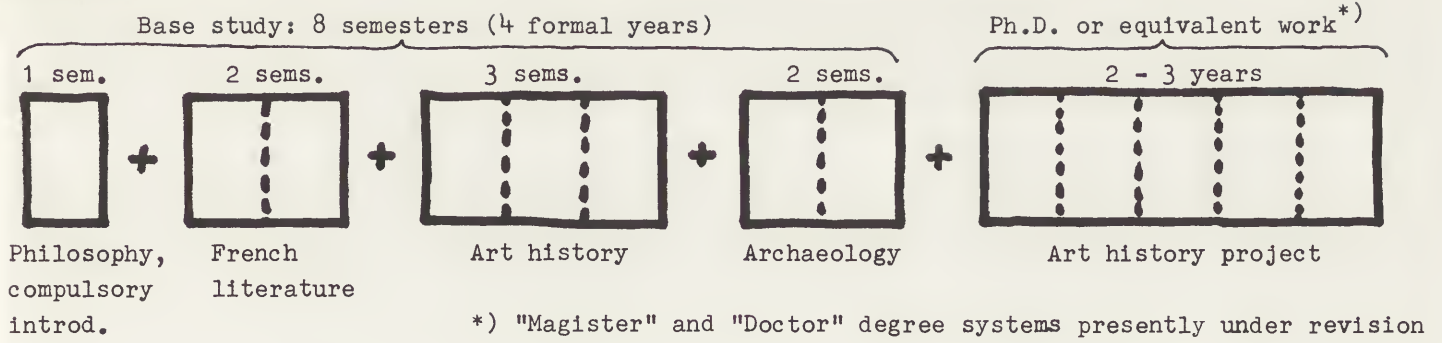
ties, i.e. from the long range of "High Schools"
and "Scientific High Schools", after a fixed
credit system. The latter system usually de-
mands more than one "external" semester in
order to equivalate one formal university se-
mester. Thus, one of the base subjects in the
sketch above, for example French literature or
Archaeology, may be substituted by, say, a
three-years' course in drawing and painting at
The National College for Art, Crafts and Design,
or by a part-time course at the High School for
Architecture.

Model I: University integration

When the committee split over the issue "Uni-
versity versus Scientific High School", it
had little to do with preferences for one type
of institution to the other; neither with
their status - which in the principle is equal
- , nor with the possibilities of establish-
ing conservation as a new teaching subject in
either of the two. The reason was two diffe-
rent ideological approaches to conservation
as such.

The committee's minority - favouring the uni-
versity - did not want to have conservation
established as a separate subject, i.e. taught
by an Institute or Department of its own along
the lines shown, for example, in London (Cour-
tauld Institute, Technology Department) or in
New York (Conservation Center). It feared this
would isolate conservation from other subjects,
to which - according to the minority - it had

to be subordinated in order to be meaningful.
The superior of these other subjects - the
minority maintained - capable of defining the
guiding lines for examination and treatment,
is the respective humanistic study (Art Histo-
ry, Archaeology, Ethnology etc.) to which the
object belongs. - "Conservation, understood as
a field of knowledge, must be a branch of each
discipline that makes use of material sources of
a perishable nature, and which society wishes
to preserve."

Faced with the way our universities are orga-
nized, the minority proposed that the study of
conservation of excavated objects be cared for
by the Institute for Archaeology; of paintings,
prints and drawings by the Institute for Art
History; of furniture, textiles etc. perhaps
by the Institute for Ethnology; and of books
and archival material maybe by the Institute
for History.

For this end, a 4-semesters' course was pro-
posed, called "Conservation theory, as applied
to the main field of study", integrated into
the combined base study in the way shown in
Figure 2 below.
The contents of this course (marked by an *) in
the sketch below), are largely those of Model
II, part A, in the majority's alternative, cf.
Figure 3): 1) Materials and their deterio-
ration, 2) Climate and transport, 3) Methods
of Examination, 4) Documentation, 5) Organiza-
tion and legislation of museums, 6) History of
technology, 7) History and Ethics of conser-

Figure 2:

Base study: 8 semesters   Ph.D. or equivalent

| 1 sem. | 3 sems. | 4 sems. | |

Philosophy,   Art History   Conservation theory,   Art history project
compulsory   as applied to art.   (optionally w. conservation)
introd.   *)
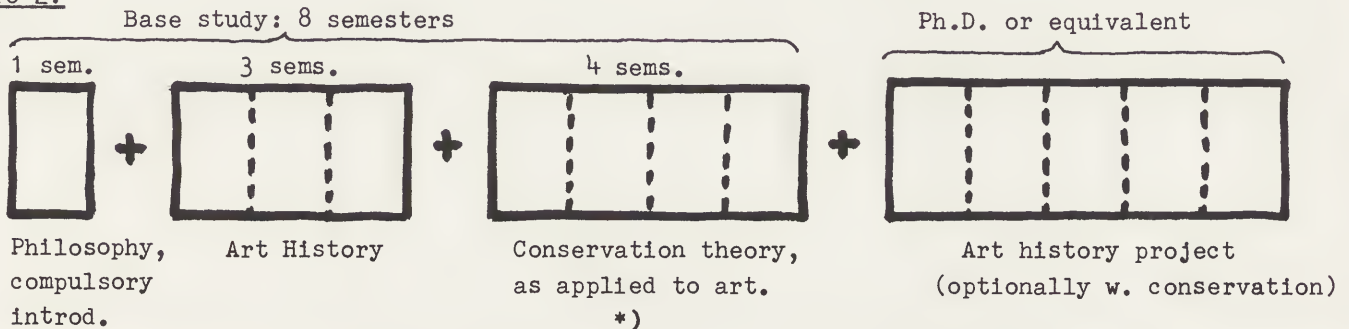
vation and restoration, and 8) Methods of con-
servation and restoration.
Subjects, as a matter of principle, are limited to
the main field of study (i.e. to art objects
in the example, Fig. 2, for a conservator of
paintings, prints and drawings).

This course is supposed to be a theoretical
one. The minority agreed that practical con-
servation must be part of the training, but
made no suggestion as to how. One of the main
ideas was that conservation must be an open
study, not primarily a field for future pro-
fessional restorers.

Model II: "Scientific High School"

While agreeing that conservators operate in a
context, not in isolation, the majority of the
committee defined the profession's position
differently than did the minority:
- Conservation is situated in a cross-road be-
tween other subjects, such as the natural sci-
ences, technology, the humanistic fields, arts
and crafts, etc. It profits from all of them,
but none of them is a priori more important
for conservation than the other.
- Conservation is a field of its own. It is
not a sum of other subjects, and it is not a
subordinate branch of other fields. Admitted-
ly, it must serve for the good of the humanis-
tic studies (like medicine serves public health),
but it cannot properly do so without being a
fully developed, independent profession (like
medicine could not if reduced to a course at
the Institute for Social Sciences, for exam-
ple).

Thus, a teaching institution for conservation
should be independent, not connected, for ex-
ample, to a particular university institute or
an art academy. This may perhaps sound over-
idealistic, but one wanted to state that such
a connection is not a requirement. A "Scienti-

fic High School" for conservation would - it
was argued - contribute to the profession's
integrity and ésprit de corps. On the other
hand, the connections to its neghbouring fields
should be articulated in the structure.

As it turned out, a study structure emerged that
looked less like the closed "High School" sys-
tem and more like a university study - with
combinations of flexible parts from other
teaching institutions, and offering its own
parts in exchange. A painting restorer may
plan his study as shown in Figure 3 below.

Only parts A, B, and C in the sketch are sup-
posed to be organized by the school.

Part A is an introductory year for all students,
regardless of the branch of conservation to be
studied afterwards. It may also be used as a
base combination for art historians, archaeolo-
gists or other future curatorial personnel -
thereby contributing to a better understanding
between curators and restorers.
Subjects are largely those in Model I (Fig. 2),
but with a general scope, plus chemistry.

Part B will give basic specialization in one
of the four following branches: paintings;
prints and drawings (plus probably books and
archival material); textiles; and objects
(archaeological and not).
Emphasis is laid on technical history as well
as methods of conservation and restoration of
the respective branch.
Theory lessons alternate with practical work.

Next follows a compulsory year of paid work in
a recognized conservation department (museum
studio or laboratory), in order to supplement
the small amount of practical work in part B.
The idea is the same as for medical doctors,
which take a compulsory year after their final
degree in other to obtain their license. How-

Figure 3:

Base study: (6 or) 8 semesters   Ph.D. or equivalent

2 sems.
A
(general)

4 sems.
B
(specialization)

2 sems.
Art history

C
Conservation project

1 year
paid work

///// = practical conservation

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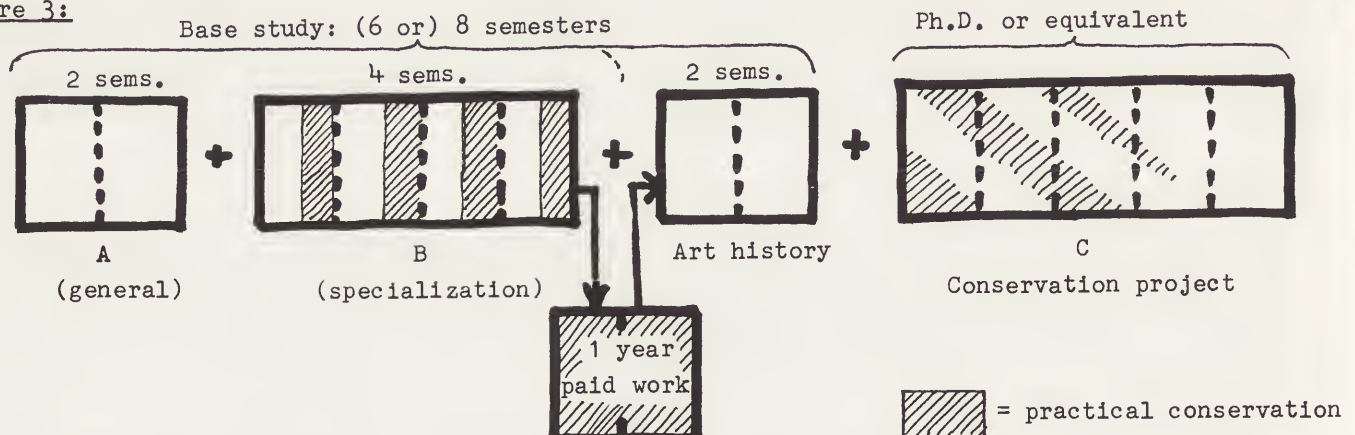
ever, it was considered better to put such a
year into an early stage of formation, instead
of in the end.

In order to form a complete base combination
of 8 formal semesters, a relevant study of 2
formal semesters at an external teaching in-
stitution must be added. This can be, for ex-
ample, a university exam (art history etc.);
a "High School" course in painting; chemical
engineering or any other relevant subject.
Many students will probably start their con-
servation study with such a subject as a
prerequisite, in which case it will be credit-
ed at this point in the study progression.

Part C will be the diploma or degree project.

Two levels of competence will be possible:
A + B (3 years), technician level, qualifying
for assistant positions; and C (6-7 years),
conservator or top level.

Concluding remarks

Both models intend to give the same formal
level of competence. In fact, Model II could
as well be realized by establishing the school
as a university institute. Its amount of prac-
tical work is not very different from that of
the dentist's study schedule, organized by the
university's Institute for Odonthology.

The difference between the two models lie in
the emphasis on conservation as the major or
minor subject of study. To say that Model I
will supply us with curators with a formal
competence to restore, while Model II will
provide restorers with a formal curatorial
competence, must be justified at least as a
face value characteristic.
Model II no doubt conforms to the guiding
lines for a definition of the conservator/
restorer's profession, set up by this working
group on the initiative of some of its most
prominent members.

An interesting point, however, is the follow-
ing: Although the part of the 7-member commit-
tee arguing for Model I is a small minority
indeed (1 person), this member, significantly
enough, was an archaeologist. The field of
archaeological conservation in Norway has a
long tradition as a branch conducted entirely
by curators - either chemists or archaeolo-
gists. Thus, the discussion of the two models
in the committee was not just one over aca-
demic subtleties, but one taking place over

firmly established local conventions.
The minority's position also was rooted in the
fact that archaeologists often are directly
engaged in excavations, and thus have a closer
relationship to conservation than, for example,
most art historians usually have. It is easier
for the latter to accept the painting restorer
as a specialist of his own.

At the moment of writing (February, 1984), the
committee's proposals are being discussed pub-
licly. The Minsitry is expected to make its
decision on the training issue upon shortly,
and will probably present it to the National
Assembly during 1984/85.

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personnel in Norway, ICOM-CC preprints, Ottawa
meeting, 1981 (81/22/4 - 1-8).

THE TRAINING OF PICTURE RESTORERS IN PHOTOGRAPHY

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SUMMARY

Initial and final conditions as well as
interesting intermediate stages in picture
restoration are, in general, photographical-
ly documented today. Besides ordinary
photos, photomacrography and photomicro-
graphy are usually used for a more detailed
documentation. Furthermore, radiation-
-diagnostic investigations into pictures
such as ultraviolet, fluorescence, infrared
and X-ray photography are an integral part
of investigatory programmes of restorers and
scientists.

It seems reasonable to enable restorers in
their training to take such photos them-
selves. The benefits are discussed, and
a special training scheme is presented that
has proved itself in the training of
certified picture restorers of tomorrow.

The training of picture restorers in photography

Today, knowledge of, and skills in, photo-
graphy are part and parcel of every modern
picture restorer. On the international
scene it is common practice to provide
reports on restoration with conclusive photo-
graphic documents that, in addition to the
initial and final condition of a restored
object, depict important intermediate
stages and details of damaged parts, special
procedures or the technical construction.

So it has become requisite to take mono-
chrome and colour photos in different light
(e.g. grazing light and transmitted light)
as well as photomacrographs and photomicro-
graphs directly at restoration work.

In cooperation with professional photo-
graphers this can be done very well; it
requires, however, centralised institutions.
More often, the restorer is compelled to
take the photos himself/herself. The long
time needed for doing so is certainly com-
pensated for by the elimination of waiting
time and dependency. Consequently, a re-
storer is now able to take such photos by
greatly saving the frequently seriously
affected objects.

There are striking reasons for a restorer to
be trained in the field of documentary photo-
graphy including photomacrography and photo-
micrography. He/she becomes fully independ-
ent only in mastering the laboratory work
such as film development, copying, enlarge-
ment etc. in addition to different ways of
taking photos.

Besides documentary photography, radiation-
-diagnostic investigations such as ultravio-
let, fluorescence, infrared and X-ray photo-
graphy have increasingly gained in impor-
tance. These techniques have become impor-
tant investigatory methods for the establish-
ment of restoration schemes and art-historic
research.

It is beneficial when a picture restorer can
take these photos himself/herself for evalua-
tion. Besides the direct benefit for resto-
ration, the sciences of art benefit especial-
ly from the fund of infrared and X-ray photos
which has come into being in a restorer's
studio.

From the afore-mentioned results the desire
to take into account photography in the
extended radiation range in the training of
picture restorers. To do so, both theoretic-
al and practical knowledge is required to
justify the subject of photography as an
integral part of the curriculum. It is
equally required to set up adequate technical
institutions where practical instructions can
be given.

Proceeding from the 5-year collegiate train-
ing of picture restorers in Dresden, ample
experience has been gained over 10 years the
following teaching programme on documentary
photography and radiation-diagnostic investi-
gations is based upon.

Documentary photography

The first year of studies conveys the neces-
sary theoretical basics for documentary pho-
tography.

This complex embraces the following subjects:
1. Photochemical essentials

- Composition and developmental characteris-
  tics of special developers of negatives
- Processing methods
- Treatment of positives - reduction in size,
  enlargement and contact copies

2. Photo-optical essentials

- Lenses and their use for special photos
- Optical accessories for photomacrography
- Lighting methods (incident, grazing and
  transmitted light)
- Cameras and their accessories
- Filters and their application

3. Instrumentation

- Enlargers and lab instruments
- Exposure meters and special metering
  techniques

The theoretical essentials taught in the
first year of studies will be applied by the
students in a 3-week practical course held
at the beginning of the second year of
studies.

Each student gets one or two paintings or one
sculpture that have to be extensively photo-
graphically documented. According to a
jointly established extent of documentation,
the student will take the required photos
himself/herself. They include several large-
-format photos of 13 x 18 cm which also
contain detailed and large sections. Photo-

micrographs are also taken of special picture sections showing the condition of the original in full.

Appropriate illumination in incipient, grazing and transmitted light clearly depicts the condition of the object under restoration.

To illustrate this, photos of details, 1:1-photos and macrophotographs up to 10:1 are taken both in monochrome and colour. The laboratory work and the preparation of documentary cards are done by the student unassisted. These cards are prepared for data processing, giving information on the conservation and restoration measures taken.

Training in photography is finished in a three-week practical course in the third year of studies. Theoretical lectures are followed by lectures on radiation-diagnostic investigations.

Ultraviolet photography

UV radiation is capable of making old natural resin-based vanishes, oil binders and protein coatings fluorescent. Fluorescence photography thus permits the detection and documentation of overprints, retouching, missing parts and thin spots. In varnish removal, the observation of fluorescence in UV light and UV photography are an important aid in order to check the degree of varnish removal.

The students are made familiar with two photographic methods:

fluorescence photography and pure UV photography. In both cases quartz glass burners are used as light sources. Corresponding to the areas of radiation, use is made of black glass filters or UV barrier filters in conjunction with colour filters. The photos are taken in all common formats.

Infrared photography

Depending on their wavelength, infrared rays are capable of penetrating paint layers, yellowed varnish and transparent coatings, making visible a covered setup of a picture and underpaints on the ground. So it is possible to detect alterations, underpaints, additions by another hand and signatures.

In the practical course, traditional infrared photography with sensitised material is practised as is infrared reflectography using an IR television camera and the display on a monitor. Infrared reflectography is often more informative, since work can be done in higher infrared wavelength ranges. Further advantages are the quickness of the method and the reduced thermal load on the object through infrared light sources.

Usually, the objects intended for investigation in the students' practical course are visually inspected with an infrared Vidicon unit, with specially interesting picture sections being marked. Subsequently, traditional infrared photos are taken of these picture sections in order to familiarise the students with this photographic technique and make a direct comparison of the two methods.

B 500 Nitraphot lamps with a colour temperature of 3200 K are used as infrared light sources when normal infrared photos are taken. Video equipment requires so-called infrared Biotherm lamps.

X-ray photography

X-rays penetrate paint layers, prime coats and panels, thus giving a complete radiograph of a work of art. For the training of students two X-ray units are available. One is a portable unit of small size that is used as a two-room system. One room houses the control unit and the other one the radiation unit. This affords maximum protection from radiation during the students' practical exercises, and eliminates the need to wear X-ray dosimeters.

X-ray units can be run by the common mains which is especially advantageous for the investigation of objects that must remain in situ. These units allow work to be done with no amplifier screens and cassettes.

The radiation dose needed for exposure results from the primary radiation of the X-ray tube. Use is made of industrial X-ray film which is available in daylight single-sheet packs. This permits X-ray investigations to be made in any place even without a dark-room which is of great value to restorers in the field and to practical courses of students.

THE TEACHING OF ORGANIC CHEMISTRY AND
CHEMISTRY OF PLASTICS AT THE FACULTY OF
OBJECT RESTORATION OF THE HUNGARIAN
ACADEMY OF FINE ARTS

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SUMMARY

The main aim of teaching science for resto-
rers is to educate them to be able to form
their questions to the chemists, to work
together with scientists, to follow the
chemical backrounds of conservation methods
written in special literature. For this aim
the organic chemistry must be tought in a
very different way than usual. To use the
restorer's creativity in teaching of che-
mical structure of organic compounds and to
bind the laboratory practice to their con-
servation-restoration practice makes the
learning easier.

The paper contents the used grouping and
order of how the necessary topics are pre-
sented for the object restorer students at
the Hungarian Academy of Fine Arts

The concept of how a subject should be
taught is determined by the training system
it fits into. Therefore prior to discussing
the process and experiences of teaching or-
ganic chemistry and chemistry of plastics
for restorers, it seems necessary to briefly
summarize how object restorers are trained
in Hungary at the academic level.

The education at academic level of Hungarian
object restorers /restorers of ceramic,
glass, metal, textile, wood, leather and so
on/ began in 1974 undertaken by way of co-
operation between the Hungarian Academy of
Fine Arts and the Institute of Conservation
and Methodology of Museums. By that time
there had been a great number of restorers
in the Hungarian museums who had been wor-
king as restorers for years but had not had
possibility to achieve academic degrees.
Training began on a part-time basis with the
aim of first providing instruction for res-
torers employed by museums. From that on 67
persons have graduated and the number of
students at present is 43. The introduction
of full-time courses is under way and will
follow in the near future.

Art history and the history of civilization
as well as some art subjects /drawing, mo-
delling/ is delivered by the lecturers of
the Hungarian Academy of Fine Arts. The
teaching of sciences, that of the theory and
practice of conservation-restoration along
with other special subjects is undertaken
by the National Centre of Museums/ this is
the new name of the Institute of Conservati-
on and Methodology of Museums/.

Taking into consideration only the chemistry
and the special subjects, the curriculum is
the following:

Year	subject, classis of theory and practice		
1st year	General and inorganic chemistry	23	6o
	Knowledge of metal materials, theory of corrosion, conservation-restoration of archaeological metal objects	24	4o
2nd year	Organic chemistry, chemistry of plastics	18 12	4o
	Knowledge of silicous materials, conservation-restoration of archaeological ceramics and glass	24	4o
3rd year 1st term	Introduction to conservation of wooden objects	6	24
	Introduction to conservation of leather objects	6	24
	Introduction to conservation of textile objects	6	24
3rd year 2nd term	Specializing in conservation-restoration of wooden/paper/textile/metal/silicous objects	Technological methods of wooden /paper/textile/ metal/ silicous objects	15	4o
		Introduction to conservation-restoration of wooden /paper / textile/ metal/ silicous objects	1o	
4th year		Investigation of wooden/ paper / textile / metal/ silicous objects	6	2o
		Conservation-restoration of wooden /paper / tex-tile / metal / silicous objects	2o	9o
		Preparing the diploma work /the students work on their doploma work also in their workshop/		6o

As regards their timetable, the students
attend the centre 2-3 days a month or have
a one- or two-week practice there. In both
case they put in 8 hours a day.

The subject of organic chemistry and che-
mistry of plastics includes all the organic
materials and plastics used by the restorer
in his everyday conservation-restoration
practice. The chemistry of museum objects
of organic basis serves as a basis for the
teaching of the conservation and restoration
of objects made of organic materials. The
composing of the curriculum is a complex
issue, not because it would be difficult to
decide what parts should be chosen from
these two fields of chemistry, but rather
because it has to be envisaged in what
sequence these topics should follow each
other and also in what kind of grouping.
The aim is in the first place not only the
encyclopaedical conveying of a branch of
chemical science, but the fact that it has
to be linked up with the practice of con-
servation - restoration.

Besides arranging the subject in a fairly unorthodox way, my aim is to take an advantage of the personal qualities of the retorers. For example the three dimensional model of the majority of the organic substances dealt with are prepared by them from plasticine or any other material. A restorer who is creative by profession, will readily take a hand and since their stereoscopic vision is good, the above exercise help them to remember the structure of organic substances as well as the changes taking place in the course of chemical reactions. The one-week laboratory practice again is fully adapted to the theory and practice of restoration.

Below I should like to give an account of the grouping and order of how the topics are presented during the classes. The topics enumerated are also the ones the students may get as questions when taking their exams at the end of the terms.

ORGANIC CHEMISTRY /2nd year, 1st term/

1/ The electron configuration of carbon in organic compounds. Characterisation of the different isomers. The major homologous series and functional groups. Excersises on the naming and recognition of organic compounds.

2/ Organic solvents

Polarity and non-polarity. Aliphatic, aromatic and cyclic hydrocarbons, alcohols, ketones, esters, ethers, chlorinated solvents, nitrogen compounds, sulphur compounds. Explanation of the solubility. A large table called "What dissolves what?" composed from special literature is completed by the students own experience.

Laboratory practice: Testing the grade of fineness of various solvents by measuring their refractive index and boiling temperature. The solvents are separated from the impurities by distillation. They test the solubility of different compounds in different solvents.

3/ Phenols and other phenolic compounds

The characteristics of vegetable tanning materials, gallic-inks, tannins and lignin. On wich museum objects are they to be found and what considerations should be taken into account during their conservation. The metal-passivation quality of tannins.

Laboratory practice: thin-layer chromatographic methods for the identification of tannins to be found on samples taken from ornamental and ethnographical textiles. Identification of tanning materials of leather objects.

4/ Formaldehyde, sugar and starch

The using of the reducing power of aldehyde functional groups for the surface plating with silver on plastic moulds of museum objects. The application of sodium gluconate for the cleaning of metals.

Laboratory practice: plating with silver, the detection of starch on museum objects, the tracing of the decomposition of cellulose and dextrose by the Fehling reaction. The production and application of sodium-gluconat in cleaning of metal.

5/ Organic acids and their derivates

The application of organic acids with fewer carbon atoms /mono-, di-, saturated and unsaturated organic acids/, citric acid, lactic acid, tartaric acid and tartarates for the cleaning and conservation of different objects. The occurence of major fatty and oleic acids. Glycerides and soaps.

Laboratory practice: Bringing about reactions confirming the unsaturated nature of different oils, produce soap and examine the cleaning effect of the latter.

6/ Organic nitrogen compounds

The characteristics of amines, amides, pyridine, urea, thiourea, azo-compounds, benzotriazole, cyanites, phtalocyanides and aminoacids as well as their application in the course of conservation. Explaining of the basis characters of amins. The bleaching effect of Kloramin T. The using of the sodium salt of ethylene-diamine-tetraacetic acid for the cleaning of metals.

Laboratory practice: bleaching of paper by Kloramin T.

7/ Surface active agents

Compounds used for wetting, washing, emulsifying, greasing, dyestuff-fixing and antistatising. Learning the trade names of Hungarian or in Hungary available foreign products, their chemical composition and application.

Laboratory practice: making fatty-alcohol-sulphate and abate some leather objects.

8/ Organic disinfectants and pesticides

The description of the disinfecting characteristics of alcohols, chlorinated and brominated hydrocarbons, nitriferous disinfectants, phenol and phenol derivates, the brands Nuvan and Eulan.

Laboratory practice: using Eulan on textile objects.

9/ Cellulose and cellulose-base objects

The chemical structure and characteristics of cellulose, the behaviour of cellulose-base materials in mediums of different pH. The effect of light, chemicals and microorganisms on cellulose-base materials. Characteristics and investigation of cotton, linen, and other vegetable fibers.

Laboratory practice: burning and solving tests, microscopic identification of the main vegetable fibers.

1o/ Protein and protein-base objects

Chemical characteristics of protein and protein-base materials. Explaining of the isoelectric point and his importance in choosing the suitable pH for cleaning and conservation. The chemical characterisation of wool, silk and other animal fibres, leather and bone. The effect of light and biological pests on natural natural protein fibres.

Laboratory practice: burning and solving tests, microscopic identification of the main animal fibres.

11/ Enzymes

The characteristics of enzymes and their application for cleaning, the removal of old sticking, with special regard to lipases, proteases and amylase.

Laboratory practice: removal of different types of stain and old glue by means of enzymes.

12/ Binding materials

After the surveying of different painting techniques, an account of binding materials is provided: oils, waxes, resins, animal and plant glues and gum with regard to their composition and chemical properties. A short introduction in the history of using various binding materials.

Laboratory practice: carrying out the infra-red spectroscopic and thin-layer chromatographic detection of several binding materials.

13/ Organic paints and dyestuffs

The description of the chemical characteristics of the historically most important paints and dyestuffs, their behaviour in mediums of different pH, the effect of different solvents and chemical reagents on theπ.

Laboratory practice: detection of red and flavonoid paints and dystuffs by thin-layer chromatography.

14/ The analysis of organic compounds

The opportunities provided by the application of optical, chromatographic and NMR methods in the examination of organic materials and organic-base objects.

Laboratory practice: visiting the Analytical Department of the technical University of Budapest where the most important apparatures are presented to the students.

CHEMISTRY OF PLASTICS /2nd year, 2nd term/

1/ The physical and chemical properties of macromolecules and plastics.

2/ The reactions of production of plastics.

3/ The decomposition of plastics and its prevention.

4/ Introduction to sticking methods. The grouping of adhesives according to the formation of the adhering bond /melts, adhesives sticking after the evaporation of solvents, binding bonds from monomers by polymerisation and polycondensation, prepolimerizied adhesives, binding by crossbinding. The description of the processes.

5/ Mould-making resins, completing materials, substances suitable for copy-making.

6/ Anti-corrosive coatings.

7/ Auxiliary products added to plastics /softenings, fillers, dyestuffs, and so on/.

8/-22/ Plastics occuring in the restorer's work: cellulose-base plastics, rubber-base plastics, polyvinyl-acetate, polyvinyl-alcohol, polyvinyl-ethers, polyvinyl-chlorid, polystyrene, polymetilmetacrylate, cyano-acrylates, polyamid, polyethylene-glycol, polyethylene, polypropylene, polyethyl-ether, polyethylen-tereftalate, ketoneresines, epoxyresines, polyesters, aminoplasts, polyurethanes, silicones.

In the course of the lectures the students come across all the products used in conservation-restoration in Hungary and during practical work of sticking and mould-making we discuss the processes taking place while binding.

At the examination of chemistry of plastics the students give an account of their knowledge of the 8-22 topics by being handed over an adhesive or mould in the packet of which carries only the label of the trade name. They are required to describe its composition, to report on what type of restoration tasks it could be used for, and how.

The teachers taking part in this training program are in a lucky position in the sense that there are not only the examination where they can measure up how the students have acquired and studied the subject.

At the end of the first year they have to carry out the conservation of an archaeological metal object. At the end of the second year their task is to conserve a ceramic or glass object. They have to handed in the whole documentation of the work with the chemical explanation of the conservation processes.

In the third year there are records on their restoration activities and technological practice.

At the end of his training the graduate restorer already having specialised in a certain field, proves his aptitude by a diploma work. In his diplomawork he is required to give a full account of the chemical properties of the object as well as a description of the physical-chemical properties of the chemicals applied, the physical-chemical backround of the cleaning and conservation process and justification of his choises.

Even if the student has not prepared tho - roughly for his examinations, at the abouve mentioned stages he cannot avoid meeting and consulting his teacher of organic chemistry. On the other hand the teacher is able to draw his student's attention if there should be any confusion or insufficient knowledge by becoming acquainted with these papers and restoration speciments.

From the fact that many of the restorers graduating from our academy do return with problems requiring the help of chemists, one might draw the conclusion that we have succeded in arousing their sense of responsibility. And I think, along with providing them with a certain amount of encyclopedical knowledge, this is the main aim of teaching sciences to restorers.

Section 22

Metals

Métaux

METALS GROUP

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              E. Andersen (Denmark)
              D. Ankner (FRG)
              J. Argo (Canada)
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Programme 1981-1984

1. Protection of finds between site of excavation
   and the laboratory.
2. Simple methods of analysis.
3. The alteration by ageing, and the treatment, of
   objects made of silver.
4. The consolidation of archaeological bronze objects.

5. Studies of patination on bronzes.
6. The treatment of outdoor bronze objects.
7. How effectively does benzotriazole actually
    stabilise active bronze disease ? Does formation
    of a complex between atacamite, etc, and BTA actual
    -ly stabilise a bronze ?
8. Comparison of mineralized wrought iron from various
    sites -such as marine, inter-tidal, fresh-water,
    land- for types of corrosion product, distribution
    of chloride, etc.
9. What is the nature of the chlorides in the mineral
    crust on iron that are not removed by washing in
    water ?
10. Corrosion and conservation of iron objects from
    above ground, below ground, and from sea or fresh
    water.
11. Electrolytic and electro-chemical treatments.
12. Corrosion inhibitors, their use and mis-use.
13. The cause, nature and treatment of the staining on
    stone below metal monuments.
14. Treatment of modern materials found ageing in
    collections.

THE DURABILITY OF INCRALAC: EXAMINATION OF A TEN YEAR OLD TREATMENT

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SUMMARY

Ten year old Incralac varnish on four outdoor gold plated bronze statues in Washington, D.C. was found to be cracked and insoluble. The Incralac was removed from the statues by softening with paint remover containing methylene chloride followed by pressurized water spray. In comparison with fresh Incralac, the ultraviolet absorption of the weathered material was greater and the benzotriazole had mostly disappeared. The infrared spectrum was little changed.

Introduction

Flanking the east end of the Arlington Memorial Bridge and the entrance to Rock Creek Parkway in Washington, D.C. there are four large gold plated bronze statues (Figure 1).

Figure 1 The gilded bronze 'Valor' on the southeast corner of the Arlington Memorial Bridge.

They were put in place in 1951. By 1971 their condition had deteriorated to the point where extensive repair and restoration was required. Corroded steel bolts, nuts, tie rods and braces were replaced with brass or bronze, accessible residual mould materials, including gypsum and sand, were removed from the interior, and cracks and pits were filled with a tin-silver solder. The original fire gilded surface was entirely removed by sandblasting. The statues were then brush plated with two layers of nickel followed by at least one layer of gold.

The final treatment in 1971 was the application of a coating of Incralac varnish. The procedure was described by Ogburn, et. al.[1] It is this coat of Incralac which is the subject of this report.

Condition of the statues in 1983

By 1983 the statues, located within 30 metres of roads carrying over 100,000 vehicles per day and under the flight path of National Airport which handles over 900 flights per day, again needed attention. Nicolas Veloz and other Park Service personnel undertook the treatment. The statues were quite dirty and there were areas of deterioration: deposition of core material, some corrosion around weepholes and seams and apparent loss of detail. Despite their poor appearance, the statues and gold plating were basically in good condition. The Incralac had failed over virtually all surfaces. There was a darkened, "painted" appearance overall and a grey cloudiness over parts of the statues which was, on closer inspection, found to be due to cracking and breakup of the Incralac layer (Figure 2). Air under the loosely adherent polygonal plates caused the cloudiness. Loss of Incralac had left some areas bare. These exposed areas were bright gold. The worst areas were those exposed to both sun and weather. Exposed areas on the north sides had an extensive craquelure, but little loss of Incralac. Only in sheltered areas did the Incralac still appear to form a coherent film, but even here there was an invisible craquelure. This was revealed by spotting dilute aqueous sodium carbonate on the lacquer film. Tests showed that electricity could be conducted between the
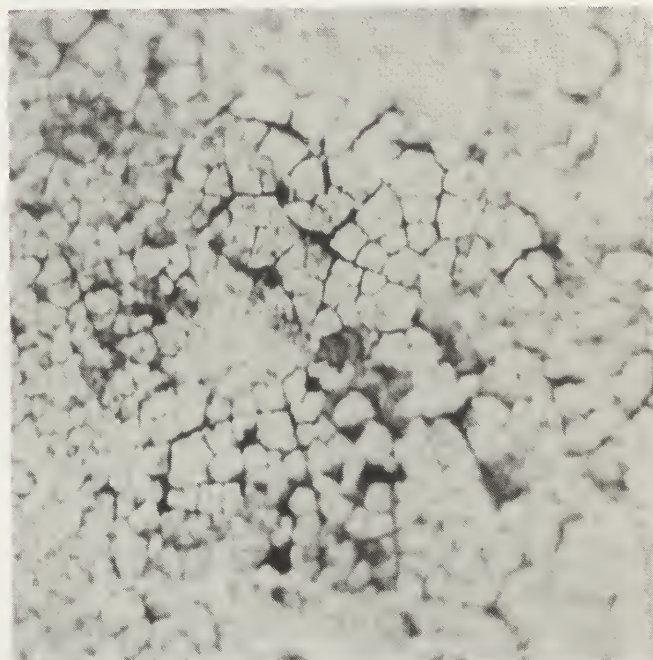
Figure 2 Fragmentary remnants of Incralac on the base of 'Valor'. This area is 12 mm across.

lacquer surface and bare metal areas, indicating that the sodium carbonate solution had penetrated the lacquer.

The 1983 Treatment

The Incralac coating proved resistant to solvents and paint strippers which readily dissolve fresh Incralac. These did not dissolve or emulsify the Incralac, but they did soften it enough to allow mechanical removal. The method found to be most effective was repeated applications of methylene chloride based paint stripper followed by cold water spray at a line pressure of 6 Meganewtons per square metre. The gold layer was adherent enough to withstand the water spray. Loss of gold was insignificant. The statues were then washed with nonionic detergent solution (Igepal CO 630), coated with an aqueous solution of benzotriazole (BTA) and finally covered with paste wax containing BTA.[2]

Incralac: Product Description

Incralac is an acrylic coating formulated for protection of copper and its alloys. It is based on Acryloid B-44 which is a co-polymer of ethyl acrylate and methyl methacrylate, available as a 40% solution in toluene. Seventy-five parts of this solution is further diluted with 20 parts toluene and 5 parts ethanol. One half part each of benzotriazole and Paraplex G-60 are also added.[3] Benzotriazole is a chelating agent used as a corrosion inhibitor. It can function both to prevent corrosion of the metal, and to protect the Incralac from the degrading effects of copper ions which diffuse into it. Paraplex G-60 is an epoxidized soyabean oil used as a levelling agent. Incralac is described in product literature as a hard, transparent acrylic having excellent resistance to ultraviolet light, which should last at least five years.[3,4]

Properties of Aged Incralac

Infrared spectra of this aged and fresh Incralac[5] are essentially the same. Their UV spectra, however, are quite different (Figure 3). The increased absorption of aged Incralac could be due either to the

Figure 3 Ultraviolet spectra of fresh and of weathered Incralac.

reaction products of degradation, or to absorption of UV absorbing pollutants from jet fuel or car exhausts, for example.

Assays by the Sherwin Williams Chemical Company, a manufacturer of BTA, found concentrations of BTA in the aged Incralac samples of less than 0.1%. This is much less than the starting concentration of 1.5%.

We compared the solubilities of fresh Incralac with those of aged Incralac taken from a vertical, north facing section of the left rump of the horse of "Music and Harvest". The results are summarized in the following table. The aged Incralac did not dissolve in any solvents. It did swell, however, in the solvents which most readily dissolved fresh Incralac. Solubility tests were conducted according to the method described by McCrone.[6]

Solvent action on fresh and aged Incralac

Solvent	Fresh insoluble	Fresh swells	Fresh soluble	Fresh very soluble	Aged insoluble	Aged swells
isooctane	x				x	
propanol	x				x	
N,N-dimethyl formamide	x				x	
diacetone alcohol	x				x	
turpentine	x				x	
dimethyl sulfoxide	x				x	
carbon disulfide	x				x	
butanol	x				x	
methyl cellosolve		x			x	
methanol		x			x	
cellosolve acetate		x			x	
carbon tetrachloride		x			x	
butyl acetate			x		x	
methyl isobutyl ketone			x		x	
1,1,1-trichloroethane			x		x	
dioxane			x		x	
ethanol			x		x	
toluene			x		x	
nitromethane			x		x	
chlorobenzene			x			x
methyl ethyl ketone			x			x
ethylene dichloride				x		x
trichloroethylene				x		x
ethyl acetate				x		x
methylene chloride				x		x
acetone				x		x

Discussion

The Incralac coating on these statues has failed as a coherent protective layer, and it has failed to remain soluble. The failure has not resulted in any major damage to the statues. Corrosion was not evident except at points such as soldered seams or casting pits where the nickel and gold plating was imperfect or at weep holes where corrosion products were washed out of the unplated interior. The plating withstood the harsh measures required to remove the insoluble Incralac.

The failure of the Incralac during ten years of outdoor exposure is not surprising. Incralac product literature suggests a film life of at least five years. The increasing insolubility of Incralac is also suggested by product literature ("In some instances it may be necessary to use a brass wire brush to loosen stubborn, old lacquer film."[4]), and it has been reported by Lafontaine.[7]

The infrared spectra indicate that there is little change in the type or number of functional groups as Incralac ages, which is why the solvents which swell the aged Incralac are solvents which also dissolve fresh Incralac. The insolubility is therefore probably due to crosslinking of polymer chains. Crosslinking of acrylics as a result of exposure to UV light is well known.[8] The acrylics commonly used in conservation are those which tend to crosslink most slowly, but one must keep in mind that insolubilization of Incralac will eventually occur.

The mechanical failure of the film may be due to thermal stress. The B-44 used to formulate Incralac is one of the harder acrylics, with a glass transition temperature of 60°C.[3] Below this temperature, B-44 becomes brittle and resistant to flow. Acrylics have a coefficient of thermal expansion about five times that of copper alloys.[9] Changes in temperature will cause differential contraction or expansion of Incralac and metal, and set up stresses within the Incralac. Crosslinking of the Incralac will make it even more brittle, and reduce its ability to relieve stress. Thermal extremes combined with crosslinking of the Incralac may eventually result in the mechanical failure observed.

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RESTORATION AND RECONSTRUCTION OF JEWELLERY OF THE IRON AGE

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SUMMARY

In 1979 the Museum of Primeval and Early History in Schönwalde (Potsdam District) investigated a casket tomb burial ground of the pre-Roman Iron Age (200 BC). The iron and bronze jewellery recovered from one of the caskets was in a state of advanced corrosion and preserved only in fragments. Prior to their treatment, these fragments were stored at a temperature of minus 25°C. This was followed by the passivation of the corrosive compounds on the iron objects by drying out in a warming cupboard at a temperature of 250°C over a period of 40 hours. After this treatment the objects were saturated in a vacuum with polymethacrylate. The jewellery parts consolidated in this manner could subsequently be treated mechanically. Finally they were coated with the protective wax (wax-fluid S). The bronze parts were first treated mechanically and then with ammonia vapour and distilled water. The drying out of the objects was followed by the vacuum saturation with an alcoholic 3 per cent benzotriazol solution. Finally the bronze parts were saturated in a vacuum with benzotriazol diluted methacrylic varnish. This was followed by a reconstruction, by which concrete statements could be deduced on the details of production technology, used materials, tools, the specialisation of fine smiths of the Iron Age, and on the ways in which this jewellery was worn.
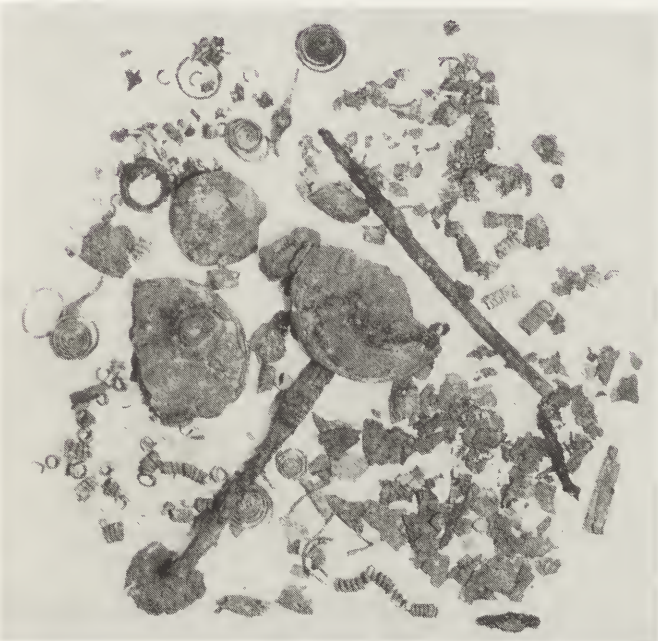
Iron Age Jewellery Before The Restoration

One of the caskets recovered in Schönwalde contained the ashes and fragments of Iron Age jewellery: an iron bronze-plated tretoil needle, remnants of bronze velum ear-rings, a number of bronze spiral coils and bronze metal sheaths   . The metal objects were stored in a refrigerator at -25°C immediately after their removal from the strata in the casket and kept there until further treatment. The initial investigations of the finds were conducted before and during the work of conservation and reconstruction. They included:
- qualitative investigations (microchemical examinations, emission spectrographic analysis); Results of the emission spectrographic analysis (qualitative): Plating of the trefoil needle: Cu, Sn; Bronze velum ear-rings: Cu, Sn, Zn, Si, Mg; spiral coils: Cu, Sn, Zn, Si, Mg, Pb; metal sheaths: Cu, Sn, Si, Mg.
- microscopic examination of the surface structure and the condition and nature of materials
 - ground and polished cross
- study of X-radiographs
- the recording of all measurements
- evaluation of technical details

Conservation and Restoration of the iron objects

The majority of the finds were deformed and partly melted by heat and badly damaged by corrosion. The microscopic investigation and microchemical analysis of the corrosion crust revealed a large number of corrosive compounds: iron oxides, iron oxide hydrates and iron chlorides (evidence of chlorides with silver nitrate), worst of all the chlorides formed as a result of deposit in acid sandy soil. It was necessary to remove or passivate these corrosion agents. In order to halt electrochemical corrosion the iron objects were dehydrated by gradual heating to 250°C in an oven. Thorough drying out of the objects was ensured by the high temperature and by prolongation of the treatment to constant weight. An average drying-out time of forty hours was ascertained by means of a number of experiments which indicated that the time required depended on the size, weight and surface structure of the various objects. The experiment with 50 iron objects showed that these objects hardly lost weight in drying times of 10 hours. During that time the objects are heated up and dried only on the surface. After that time the drying process takes place more slowly. Up to a duration of 35 hours there was a constant reducation in weight. After this drying process the weight of the objects remained constant following a renewed drying of 5 hours.

X-ray examination of the archaeological iron objects revealed that the jewellery was almost completely corroded. After drying out and before further mechanical treatment it became necessary to consolidate the fragments of the trefoil needle. For this purpose the iron parts were immersed in polymethacrylate monomer (EBM) plus catalyst and saturated under vacuum at 6.7 HPa (5 Torr) for 30 minutes. Following this saturation the consolidant was polymerised in the oven at 30°C for 3 days. The parts consolidated in this way could subsequently be treated mechanically with fine abrasives. Missing parts were substituted by polymethacrylate and finally the objects were coated with a protective cover of a wax suspension of hydrocarbon waxes. The solid wax film is constant between -50°C and +90°C.

Trefoil Needle Before The Restoration

Conservation and Restoration of the bronze objects

No treatment of the bronze plating of the trefoil needle, mineralised by corrosion, was necessary apart from saturation with benzotriazole.

The poor state of preservation of the bronze jewellery did not allow use of chemical treatments to dissolve or to remove completely the corrosion strata. All of the bronze objects were treated mechnically, partly under the microscope, with scalpel, glass-fibre pencil and fine abrasives. Subsequently the objects were treated in ammonia vapour. The copper complex salts (amines) were removed with distilled water and after drying out in an oven the bronze objects were saturated in vacuum with a 3 per cent solution of benzotriazole in ethanol. After the stabilization of the benzotriazole complexes at a temperature of 60°C (Bibliography: Cotton, J.B.; Scholes, I.R.;: Benzotriasols and Related Compounds As Corrosion Inhibitors For Copper. Brit. Corros. 2nd year of publication (1967), p. 1-5) a coating of polymethacrylate varnish (Piaflex LT41) with an addition of benzotriazole was applied under vacuum.

Bronze Metal Sheaths Before The Restoration
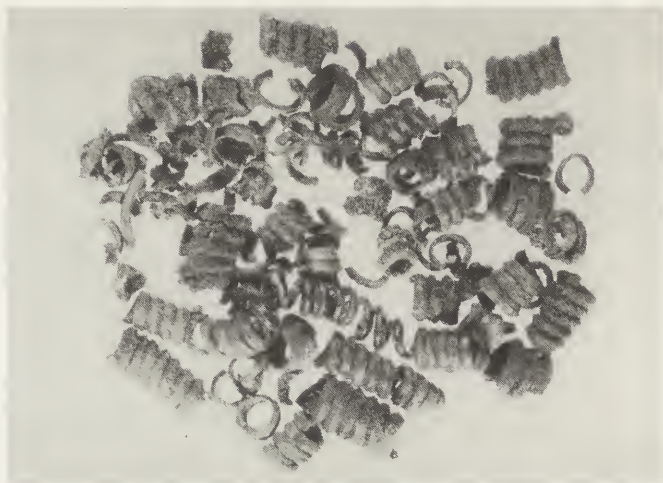
Bronze Wire Spiral Coils Before The Restoration

Reconstruction of the trefoil needle

The surface structure of the iron needle and the almost completely melted off thin bronze plating allows the conclusion that the objects had been exposed to temperatures of approximately 800° - 900°C (secondary funeral pile). The original, now consists of fragments of the original bronze-plated iron needle. The iron came from bog iron ore (0.65% phosphorus found by spectrophotometrical analysis to be phosphomolybdic blue) of low-grade quality. The reconstruction work was done using processes believed to have been used in making the original. The needle, roughly 45cm in length, had been forged out of a piece of iron in glowing condition. The production of the foils, roughly 80mm in size, demanded iron foil beaten out to a diameter of 1.6mm. The holes required for the rivets were poked into the red-hot metal with the aid of a steel pin. The separate parts were joined with iron rivets.

A copper-zinc alloy was used for the bronze plating of the reconstruction. In the original the bronze plate was cold-forged from a piece of bronze. This small qualtity of metal can well be forged into sheet metal. Bronze sheet metal of this minute diameter can only be produced by forging. The plates for the reproduction were pretreated by annealing and subsequent tempering with water and then finished and ornamented by means of chasing and engraving techniques. Chasing cement had to be used for this work. We may suppose that the original plated needles had undoubtedly used pitch extracted by distillation from birch bark. Lead, wood, rosin, may also be used for chasing work. The metal plates were pressed into the heated cement and hammered with cold sets to produce a line drawing of the ornament, as recognisable as the original, that was engraved with an iron or flint needle. After reheating the cement, the plate was turned over and given relief with modelling punches. Ornaments on bronze may be worked with the aid of bronze punches hardened with bronze tools, even if they consist of the same alloy. The Iron Age smith presumably used sharp-cornered iron punching chisels with wide cutting edges for cutting out the circular bronze plates from sheet metal. Apart from forged iron tools, case-hardened bronze tools could also be used for this working technique. In experiments, hammer-hardened bronze tools made of an alloy with 5 to 10 per cent tin proved to be best suited to the purpose. Finally, the trefoil needle was finished smooth and the metal plates were polished. Fine-grained sandstone, slate, chalk or leather may be used for the final treatment of the surface. The reconstructed

disks were given a smooth, compact surface by
polishing with fine-grain sand and subsequent
finish with chalk and leather.
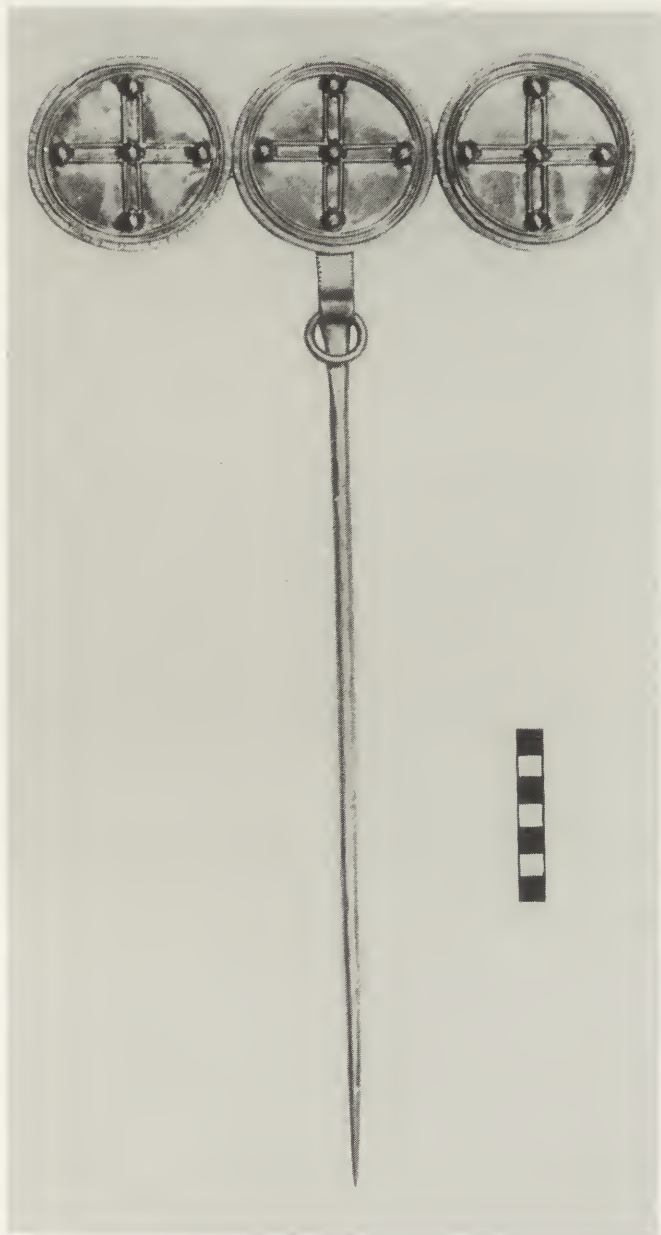
Reconstruction Of The Trefoil Needle Averse

Reconstruction Of The Trefoil Needle Revers

Reconstruction of the bronze ear-rings
Copper was used for the reconstructions of
the preserved fragments of the original ob-
jects that had been greatly deformed by heat.
Even for objects in this condition it is
possible to ascertain which parts were ori-
ginally cast and which had been forged. The
cast parts, that is, those not compressed by
hammerforging or finish, are brittle: they
crumble if exposed to intense heat and leave
hardly any fused residue. The forged parts,
such as wire, needles, spirals, etc, resist
even great heat for a time but ultimately
melt to form a fused mass. The original ear-
rings were probably made of a copper-tin
alloy containing roughly 5 to 10 per cent
tin. This alloy has the best properties for
cold working. To finish the thin-gauge metal
in chasing cement is possible but the best
reproductions were obtained by the use of a
hollowed-out wooden die into which the an-
nealed metal is forced. The metal parts can
only be driven into the depressions of the
die with a spherical groove-hammer or with a
ball-ended punch.

Reconstruction Of The Bronze Metal Sheaths
And Bronze Wire Spiral Coils
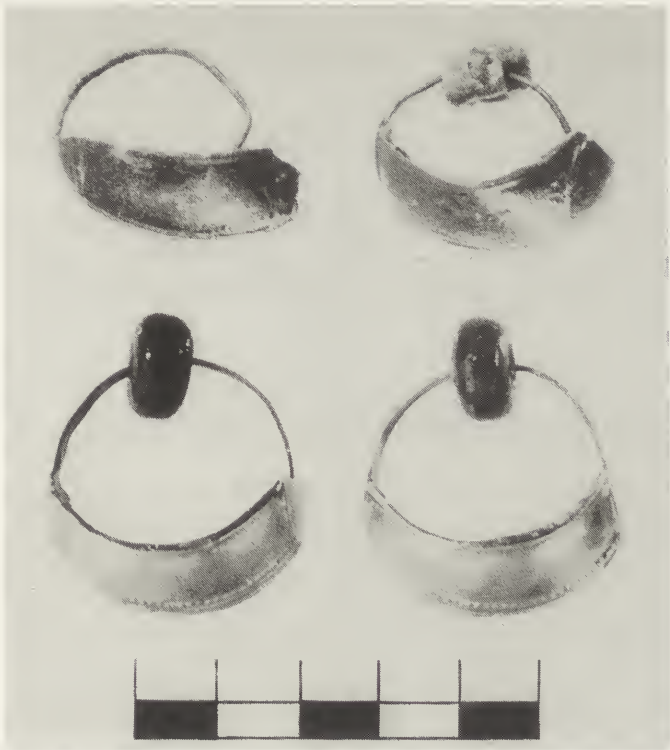
Ear Rings Past The Restoration And Recon-
struction

Reconstruction of the bronze spiral coils

No evidence for organic connecting elements
between and in the metal and spiral coils
could be found in the originals. Microscopic
investigations revealed that the bronze
wire, D-shaped in section, of the original
coils (the wire measures approx. 0.5 x 2.2mm)
was forged from a cast-bronze rod. In the
reconstruction a copper wire, round in cross-
section, was made by the same procedure and
subsequently was hammered into a D-shaped
groove, previously cut into a bronze plate.
It was given a more or less even profile by
the hollow in the die. The grooves seen
running lengthwise on the original were
either cut or polished or cast into the pro-
file worked into the metal plate. On no
account do they represent evidence for use of
a die-plate. Compared with forged wires
string wires show less deviations in diameter
and surface structure.

Reconstruction of the bronze metal sheats

The metal parts, made of a copper-zinc alloy
0.3mm thick, were also fixed to chasing ce-
ment and the rib-shaped ornaments were worked
in with cold sets and modelling punches.
Measuring and microscopic examinations of
conspicuous processing marks on the walls
of boreholes showed that these had been
bored by a pointed-tip drill. There are no
signs of the compression and clinching marks
on the edges of the holes that are typical
of cutting out by punching chisels. In pre-
liminary experiments a pointed-tip drill
made of forged iron (cutting angle 40°)
easily drilled holes into thin metal. Under
the microscope the bored holes showed the
same marks of working that were seen on the
original. Machining techniques such as
boring, engraving, tremolo-engraved orna-
ment, sawing or turning cannot be done with
bronze tools on copper alloys.
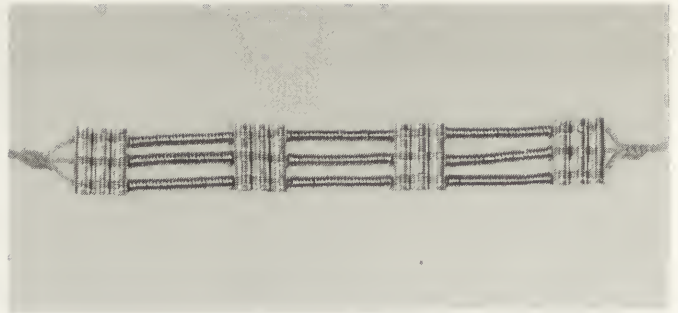
IRON CONSERVATION AT THE NATIONAL MUSEUM OF
COPENHAGEN - PAST AND PRESENT

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SUMMARY

Local conditions influencing the state of mu-
seum specimens set the frame for possible
methods of treatment. In Denmark these speci-
fic conditions have determined the use of
conservation methods involving heating proce-
dures and electrolytic treatments of archae-
ological and historical iron.

The history of conservation methods applied
and developed from 1898 until today is de-
scribed and their usefulness is discussed.
This leads to the conclusion that heating
methods are indispensable for certain cate-
gories of iron objects, but that modifica-
tions and entirely new ways are needed. Gase-
ous and liquid reduction methods are especial-
ly favoured. Some possible solutions are sug-
gested, e.g. hydrogen reduction, plasma reduc-
tion, electrolytic reduction and sulphite re-
duction. The use of inhibitors is also taken
into consideration.

INTRODUCTION

As with all museum collections, the collec-
tions of the National Museum in Copenhagen
have special requirements and demand special
considerations in the field of conservation,
depending on local conditions.

The geology of Denmark, the climate, the mod-
ern intensive farming, industrial pollution,
pre-historic and historical habits and customs
(e.g. burial traditions), present the conser-
vator with specific problems. In other words:
the local circumstances influence the nature
of the objects, their state of preservation
and thus the type of treatment which can be
employed.

Apart from this, many important archaeologi-
cal, historical and ethnographical objects,
both from Denmark and from abroad, have been
part of the museum's collections for a consid-
erable time. This means that re-conservation
and the repair of accidental damage, besides
"ordinary" first time treatment, are required.
In this connection it is also very important
to have a knowledge of the old procedures and
their consequences.

Being an old institution, the National Museum
has of course a long tradition of conserva-
tion, which in many ways influences today's
work in the Conservation Departments.

The purpose of this paper is to discuss some
of the problems involved in the conservation
of iron, and to describe the methods currently
in use, as well as possible future develop-
ments. Iron has been selected from other met-
als, because it is a difficult and interesting
material which constitutes a large part of

Danish finds.

HISTORY

The first records of conservation date from
1898 and are written by Conservator Gustav
Rosenberg. He was in contact with Dr. Rathgen
in Berlin which means that, as early as 1898,
he knew and used many of the methods mentioned
and recommended in Rathgen's manual (handbook)
published the same year (1).

The notes of Rosenberg show that well-pre-
served archaeological iron from then on was
washed out, boiled in paraffin or vacuum-
treated with dammar-resin or celluloid-
lacquer.

As an alternative, unstable iron was subjected
to Krefting's electro-chemical treatment (me-
tallic zinc and NaOH-solution). This method
was also employed in exposing hidden decora-
tions, e.g. inscriptions and inlays (1).

In the notes from the following years, howev-
er, one meets an increasing dissatisfaction
with the appearance as well as the stability
of objects treated in the above mentioned
ways.

For ethical and aesthetical reasons Rosenberg
was reluctant to strip heavily corroded or in-
layed iron. The objects often became shapeless
after the treatment, or the inlays would easi-
ly drop out.

From the year 1907 we find a note that such
fragile objects should only be treated elec-
trolytically, if stripping was found necessary
for the stability of the objects.

Krefting's method, however, was continuously
employed in the treatment of superficially
corroded iron until at least 1950.

Rosenberg's notes from the first decade of the
century reveal that he had to perform an in-
creasing number of reconservations due to the
instability of objects which had only been
washed out before impregnation. This treatment
obviously couldn't secure the long term stabi-
lity of the objects.

These problems, and similar ones in the con-
servation of archaeological bronzes made
Rosenberg re-think the matter.

The result of his reflections was the launch-
ing in 1917 of the electro-chemical method of
stabilization, applied to bronzes (Al-foil at-
tached with gelatine and exposed to high RH),
and the "heating to redness-method", applied
to unstable iron objects (2).

This method of stabilizing archaeological iron
became the standard procedure of the museum
and was employed with only a few modifications
from about 1917 - 1977/78.

The objects were heated to red heat at $800^{\circ}C$
for about 15 minutes - 2 hours in ordinary at-
mospheric air. While still hot, they were then
plunged into a saturated sodium or potassium
carbonate solution.

This procedure opens the crevices of the ob-
ject and remaining soluble salts are leached
into the solution. After that the objects are
subjected to washing.

These after-treatments are needed because the
short period of heating is unable to remove
all unwanted compounds by evaporation. The ob-
jects are then dried and finally impregnated

with wax.

This method has been much criticized, especially because of the fact that the high temperature in the oven destroys all evidence of original structure of the metal.

The criticism of Rosenberg's procedures prompted Conservator Børge Brorson Christensen to write in defence of the method (3).

He emphasized that the method is especially well suited for the treatment of heavily corroded iron, because the "heating to redness" makes the otherwise hard layers of corrosion easily accessible to mechanical removal. It also makes it possible to recover the original shape and surface of the object. He also pointed out that most Danish pre-historical iron objects are so corroded that almost no original structures can be found. Besides, this pre-historic iron in Denmark comes very often from cremation graves and is annealed already when found.

Børge Brorson Christensen's support of Rosenberg's method does not deal with the question of stability.

This, however, was the main interest of the investigations carried out by Eva Salomonsen as an examination paper for the Danish School of Conservation in Copenhagen 1976/77 (4).

She clearly showed that the method was not as flawless as many Danish conservators tended to think. It was revealed that almost 20% of all objects treated by Rosenberg's method since 1917 were unstable. This fact couldn't be ascribed entirely to unsatisfactory storage conditions. Part of the explanation was to be found in the procedure of conservation itself. The carbonate treatment and the process of washing were found to be the crucial points, because too many hygroscopic salts remained in the objects. Besides this, it was found that the often brick-red appearance of many objects was aesthetically unattractive.

The Conservation Department for Archaeological Finds therefore decided to adopt a modification of the original method.

This modification did not alter the basic two-step procedure.

The only significant change in the oven-treatment was a replacement of atmospheric air by nitrogen. This was inspired by the results of experiments carried out in connection with the Wasa-project in Stockholm (5, 6).

It should be mentioned that the use of hydrogen was avoided for safety reasons.

The advantages of this procedure are that objects as well as corrosion products become uniformly dark in colour and mechanical cleaning is also made easier because the corrosion products become softer.

The new procedure of de-salination was an adoption of the Lithium-hydroxide method (7).

During the first year after the introduction of the new method, it was discovered that most of the objects showed themselves to be unstable immediately after treatment.

Once again an investigation was carried out, and as a result the Lithium-hydroxide method was abandoned, because the treated objects were still full of hygroscopic salts.

This method is probably not suitable for the kind of highly corroded objects which consti-

tute the main part of Danish archaeological finds.

Other investigations concerning this matter have concluded that this opinion is not entirely wrong (8, 9).

It was, however, demonstrated that by prolonging the time of heating, it was possible to avoid de-salination in a liquid medium, because most of the hygroscopic salts in the iron evaporated (7, 10).

The advantages of this procedure are that one saves time and that the objects can be absolutely dry when coated by one of the modern, impervious lacquers and waxes (e.g. acrylic lacquers and modern types of micro-crystalline wax).

It was ascertained that the last residues of water of crystallization only evaporate from the corrosion products at a temperature of about $500^{\circ}C$ and over a long period of heating.

The use of an inhibitor was tried after the heating in order to passivate the salts assumed to be left in the objects (sodium-petroleum-sulphonate in the CPD 32 dewatering fluid from B.P.).

This procedure was, however, abandoned temporarily because the following mechanical cleaning made it undesirable for health reasons.

For the time being it is difficult to predict the long term stability of the objects only heated in inert atmosphere, and without any inhibitor treatment, but experiments in a humidity chamber have shown promising results (RH~85%).

Today heating is used primarily as a method for stabilizing objects which need re-heating, objects from cremation graves and objects with an insignificant metallic core. Sometimes heating is also employed as a means of stabilization in the treatment of objects that have been otherwise conserved in the past. But the method is only applied when the objects are so threatened by immediate decay that no other solution is possible. In addition, large quantities of small uniform objects - e.g. nails and rivets - are heated when unstable.

Objects considered unique, wrought iron with a considerable metallic core, cast iron or iron objects attached to other materials (i.e. leather, bone, textiles) are not heated (11).

Superficially corroded iron, iron from early modern times and marine iron is almost always treated electrolytically. The first equipment for electrolysis was procured in 1950 and has since been modernized. Cleaning and/or de-salination is performed as required. Insignificant corrosion on composite objects can also be removed chemically or with an air-abrasive.

In order to protect "out-door" objects cleaned in the above mentioned ways, several layers of industrial paint are applied (red lead). "Indoor" objects are protected by tannin, phosphatizing and impervious alkyd and acrylic lacquers, and micro-crystalline wax.

THE FUTURE OF IRON CONSERVATION AT THE NATIONAL MUSEUM

The following suggestions are only meant as a preliminary sketch of some of the possible ways of conserving iron in the future.

As will be seen from this historical outline, the main problems in the conservation of Danish iron material concentrate on two points of which the latter presents greater obstacles than the former.

The two points are:

1. Passivation and surface protection of objects after heat-treatment.

2. Cleaning and preservation of objects which for various reasons cannot be heated.

For 1, it is now desirable to re-open investigations into the possible use of inhibitors. In addition, investigations into the use of waxes and lacquers are still needed, because surface protection, as well as support of hollow and otherwise fragile objects, is required.

For objects of type 2, the following possibilities are considered:

a) Sulphite reduction, which renders heating unnecessary. This method could be useful in the treatment of moderately corroded objects, retaining a solid metallic core, or objects suspected of having received a hardening treatment. It is not expected that objects with inlays and organic attachments should be treated in this way (11, 12).

b) Hydrogen gas reduction, so that it is possible to treat objects using temperatures not exceeding about 600°C. In this way metallurgical evidence in cast iron is not necessarily destroyed all together (6, 12, 13).

Research carried out at the Danish University for Technical Sciences has also shown that the hydrogen reduction method secures a reasonable stability for certain wrought and cast iron objects at temperatures of about 300 - 400°C with a prolonged heating time (14, 10).

Objects with certain inlays and certain organic attachments can be treated in this way.

c) Plasma reduction carried out on early modern material is still at an experimental stage. For the time being it is too early to say anything conclusive about the practical applications of this very complicated procedure, but some interesting results have been brought about, especially in silver.

CONCLUSION

Annealing methods - in spite of their shortcomings - are indispensable as stabilizers of large parts of Danish archaeological iron. However, it is acknowledged that modifications to these and entirely new ways are necessary in order to make our collections last and to be of scientific value to our successors.

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MICROMETALLOGRAPHICAL EXAMINATION AND CONSERVATIVE TREATMENT OF EARLY MEDIEVAL SILVER CHALICE AND PATEN

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ABSTRACT

A set of chalice and paten found by archaeo-logical excavations under the Cathedral at Po-znań in 1953, dating back to the turn of the XI to XII century, silver, chalice forged and chiselled, paten forged, chiselled and repous-sé, has been micrometallographically investi-gated and treated. Investigation comprised e-mission spectrography, micrometallography with SEM and EM observations revealed many structu-ral, substantial and technical characteristics as well as details concerning mechanism and ef-fects of corrosion. Conservation covered dis-mantling of chalice and paten from warped sup-porting structures from previous conservation and the repeated assembly on new support of polyester-fiberglassfabric laminate.

1. INTRODUCTION

In the course of archaeological excavation un-der the Cathedral in Poznań, carried out in 1953-1956 many remains of early medieval bu-rials of lay and clergydignitaries have been found and among others precious pieces of jewe-llery and goldsmith´s works, early romanesque silver chalice, 9,5 cm high, forged and chisel-led, and a silver paten, 9,7 cm diameter, for-ged, chiselled and repoussé, both dating back to the turn of XI to XII century. These ob-jects have been attributed to a bishop´s fu-nerary endowment. As extremely rare, valuable objects of historic importance, they were in-vestigated, treated and exposed in museum.The state of preservation of chalice and paten af-ter excavation was very bad; they were bruised folded, broken into fragments, corroded in so-me places completely in whole cross section , covered with thick deposits of beige-violet compact, unctuous crusts.

2. FIRST CONSERVATION

The first conservation has been carried out in 1960-61 by State Enterprise for Monuments Con-servation in Warsaw. The treatment consisted in removing of corrosion deposits, cleaning , backfolding if distorted fragments, assembling of fragments and filling up defects. Deposits of corrosion products have been removed by me-chanical method. The tools were sharp needles and small chisels mounted in wooden handles.

The operation has been made partly under medi-cal stereomicroscope by magnification 4 - 25x. Tarnished surface and stains have been cleaned by using a little French chalk diluted with methylated spirit containing a few drops of a-mmonium thiosulphate and thiourea solution. The backfolding of distored fragments is not easy task that appears to be, because silver becomes brittle on ageing, and mechanical ma-nipulation has been undertaken by careful anne-aling and tooling back to shape by means of wooden stakes, levers, small mallets and sha-ped wooden supports covered with leather. The first operation in order to restore the origi-nal shape of chalice and paten was to get the edges of fragments and cracks to meet exactly, then thick solution of butyl methacrylate co-polymer and strips of thin PBM sheet have been used to glue and to consolidate the objects as well as to fill up the defects. In the years 1960-1970 it was the commonly applied method of.conserving goldsmith´s antique objects.

3. DEFORMATION OF ACRYLIC SUPPORT

After some 15 years symptoms of deformation of acrylic supporting structure which warped came into sight. Attemps made in order to escape un-pleasant symptoms have been effectless. The new conservative treatment was decided in 1981 following new achievements in restoration of such excavated, burial silver objects in a cru-shed and very brittle condition.

4. MICROMETALLOGRAPHICAL RESEARCH

Micrometallographical research included follo-wing examinations:
a/ X-ray defectoradiography.
b/ Revising spectral emission analysis.
c/ Metallography by means of optical microsco-pe.
d/ Determination of microhardness.
e/ Metallography by means of E.M. and S.E.M.
f/ Electron microprobe.

a/ X-ray defectoradiography is particularly u-seful for assesing the internal condition of a silverobject. Silverchlorides and oxides are relatively much more transparent to x-rays than the solid metal, and x-radiographs reveal the distribution and extent of corrosion more certainly and directly and estimate the depth of pitting. Examination has been carried out by an x-ray defectoscope Baltospot 125.

b/ Spectral analysis has been carried out by means of Zeiss Q 24 Forschungspectrograph , spark induction. The results are shown in the

Table 1. In analysing the samples were prepared by the standard procedure. The data show great difference between composition of silver alloys in chalice and paten and the considerable heterogeneity of silver.

Table No 1
Results of emission spectral analysis.

| Object | Contents % weight | | | |
	Cu	Zn	Pb	Fe
Paten	30,0	0,0	3,0	0,10
	25,3	0,0	1,95	-
	18,2	0,0	2,6	-
Chalice	10,0	0,0	2,0	0,05
	8,7	0,0	1,65	-

c,d,e/ Micrometallography has been carried out by means of a metallographic optical microscope Zeiss Neophot with device for microhardness by magnification 630 x, scanning electron microscope Cambridge SEM and electron microscope IEOL /imprint in plastic/. Transverse sections polished samples from chalice and paten illustrate presence of silver-copper alloy of intermediate degree of homogeneity, with differences of paten in comparison with chalice. The microhardness in the middle of the grain and within displacement of boundaries is different and amounts:

H_m near displaced grain boundaries=80±4
H_m in the middle of grains   = 76±5

Chalice was made of the silver-copper-lead alloy. The concentration of copper was less then in the paten. The metal is corroded in the high degree. Metallographical examination showed the corrosion deposits in microcracks and intercrystalline corrosion paths along the grain boundaries.

The microstructure of the sample was rather homogenous with the large grains. The small amount of rich copper phase was also visible. These large grains formed after the last annealing by secondary recrystallisation.

The fine inclusions were elongated in the direction of plastic deformation, no visible precipitation of copper was observed under SEM at higher magnification the grain boundaries have strange outlines. These grain boundaries displacements could be connected with discontinous copper precipitation. The microprobe analysis gave result copper content 2,2%. The precipitation of copper could be retarded by presence of lead.

The brittleness of silver in chalice could be due to:

- the intercrystalline corrosion,
- the copper precipitation,
- the lead inclusions in metal.

Paten similar as chalice was made of the silver-copper-lead alloy. The metal was corroded in the high degree. One can observe under microscope the deposits of corrosion products along the boundaries and in microcracks.

The microstructure of this sample was rather homogenous with the copper rich phases at the grain boundaries. The amount of the copper rich phase was less than one could expect from the chemical composition. The microprobe analysis gave a copper content of 8,8% only. It means that concentration of copper in the alloy of paten varies greatly.

Large complex inclusions were elongated in the direction of plastic deformation. The examination under SEM permited to identify the small elongated lead inclusions. After the cold work metal was annealed. No precipitation of copper and grain boundaries displacements were observed.

The brittleness of silver in paten was due to
- intercrystalline corrosion,
- lead precipitation in the alloy.

f/ Electron microprobe has been carried out by accelerating voltage 20 keV, by current 0,05 A, beam diameter 1 micron, line $CuK_{\alpha 1}$
The results are shown in the Table No 2.

Table No 2

Microprobe analysis.

Object	Content % Cu		
Paten	11,6 , 18,5 8,2x		
Chalice	8,4 , 8,1 , 7,4 2,2xx		

x = within grain   xx = along grainboundaries.

5. NEW RESTORATION

The new conservative treatment consisted in:
a/ Dismantling of acrylic support.
b/ Removing of swollen acrylic remains and cleaning.
c/ Restoring of the shape and mounting on a new polyester-fibreglassfabric support on silicon pattern match.

a/ Dismantling of acrylic supporting structure has been carried out by partly dissolution and swelling of acrylic resin in acetone.

b/ <u>Removing</u> of swollen acrylic remains and
cleaning has been made in mechanical way by
picking, chipping and scraping using a simple
kit of small needles, chisels and scrapers
self made, mounted in wooden handles, ade -
quate for these purposes.This is a labour of
accuracy, and patience. The operator must ad-
vance slowly, piece by piece, observing under
the medical stereomicroscope.

c/ <u>Restoring</u> of the shape has been performed
by careful tooling with special wooden sta -
kes, levers, mallets of hard-wood and bone
on pattern match. The first operation was to
restore the shapes of fragments by dealing
with the edges and cracks to meet exactly,
then patches of very thin fibreglassfabric
were applied and fixed with polyester resin
permanently in position across the cracks on
the underside.

This was a long and exacting operation, but
well worth, because as the work advanced the
defects and cracks disappeared and the objects
became noticeably stronger and more rigid.The
pattern matches for the objects in like man-
ner as shoemaker's lasts have been made of wo-
od covered with silicon rubber. Consolidation
of objects and completion of defects have
been carried out in the same operation cal -
led lamination.

Some tenths years ago acrylic supporting stru-
ctures and completions were preferable, trans-
parent and colourless. Nowaday we like better
the supports and comletions tarnished a lit-
tle in order to integrate external appearan -
ce of the object.

In our case the surfaces of completions have
been tarnished a little with fine silver pow-
der called "silverflakes".

AN APPROACH TO HANDLING LARGE QUANTITIES OF ARCHAEOLOGICAL IRON

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SUMMARY

Conservation of iron objects must begin at the time of excavation. An integral part of the success of a conservation programme is proper field handling to ensure that maximum information is recorded for each object, that post-excavation storage is compatible with a planned conservation treatment and that systems for both recording and storage are compatible with the needs of the archaeologist during the period between excavation and treatment. This paper discusses an approach to the handling of large quantities of archaeological iron. The excavation of a 16th century Spanish Basque whaling station on the coast of Labrador is used as an example of the successful application of a conservation programme in which in-field recording and storage played an integral part.

INTRODUCTION

Conservators dealing with archaeological collections should all be familiar with the problems that archaeological iron presents. Iron is an inherently unstable material, but due to the ease by which it is refined and shaped, and its versatility, iron has been widely used for the past 3,000 years. Sites on which iron is preserved not only present the basic conservation problem of "how to stabilize", but also a collection management problem of how to cope effectively with a large volume of unstable material in a very short period of time.

The way iron is handled immediately after excavation will affect any future treatments. Because of the quantity of iron that may be recovered from some sites, and the fact that initially it may not appear to undergo any drastic changes on excavation, iron is often not given any special care. This invariably leads to objects' returning from the field in miscellaneous bags or boxes, to be put into "storage" until someone gets around to looking at them to write a report. By this stage, the collection may be exhibiting signs of instability: surfaces may be spalling, some objects may crumble on handling, formation of new corrosion might be noted. The objects will have lost their original integrity and conservation treatments left to this stage may not be successful.

A conservator of archaeological materials has a role to play long before this stage is reached. The conservator must develop, with the archaeologist, a total plan for conservation that will encompass recording, materials characterization and field storage in addition to the eventual treatment.

DEVELOPING A PLAN

It has been stressed in the conservation literature[1,2,3,4] that upon excavation, material undergoes change in response to varying conditions of humidity, concentrations of oxygen, light levels and temperature. This change may be rapid and irreversibly damaging, as in the desiccation of water-logged wood[5], or it may take place relatively slowly so that the effects are not immediately obvious - such as the alteration of corrosion products on metal[2]. The aim of a conservator of archaeological material is to control the inevitable alteration and to direct changes in the chemistry of excavated material. In order to do this, the conservator must have some control over the method by which objects are retrieved from a given environment. This control must complement the needs of an archaeologist to gain as much information as possible about the objects.

Recording

Recording conservation data in the field is one area which overlaps with archaeology and enhances the data base of a collection[6].

The word "collection" is important when considering a recording system for archaeological material. Often, if viewed only as individual artifacts, archaeological objects may not appear significant. Iron may be present as unpromising lumps of corrosion, broken nails, discarded bits of broken tools. The function of bits of iron may be impossible to pinpoint since chances are high that other materials that were associated with the iron have been destroyed. Although it is possible to plot distribution of artifacts in a site, when dealing with highly mineralized metal it may be difficult to determine and plot their function or to understand subtle variations across a site, (such as style and size of nails used in construction) or to detect patterns of destruction.

It is difficult to visually record and describe collections of corroded iron. X-radiography, a technique routinely used by conservators to record details of individual objects[7], can be extended to collections. X-raying together all the ambiguous blobs of iron and fragments from various areas of a site will give the archaeologist an accurate visual picture of trends across a site. This is useful for the conservator too, since differences in condition resulting from microenvironments will be obvious from the x-ray results. Another value of radiographs is that the archaeologist can have a visual record of his collection at his fingertips, with approximate sizes recorded even when the objects themselves have disappeared into holding or treatment solutions. The other obvious value of such a record is that should conservation be less than successful (always a possibility when dealing with iron), then a record will remain.

Storage

The information provided by characterization is fundamental to selecting a storage system and a treatment method for iron. If this type of information were routinely acquired then instances of selecting inappropriate pre-treatment storage conditions or conservation treatments would be reduced[8].

Metal corrosion products, in particular, reflect burial environment and if a conservator is familiar with soil chemistry (or marine chemistry) he will often be able to predict to some extent how materials will have altered during burial. Ideally, observations and logical deductions based on the chemistry of a given site should be followed by sampling to accurately determine corrosion products, mineralization and levels of soluble salts[3,4,9]. The technology for this type of analysis is accessible to most archaeologists and conservators, at universities, for example. If a site promises to produce a lot of material requiring conservation, this type of analysis should be planned for well ahead of the field season so that it can be done at an early stage of the excavation, when planning of the storage

conditions still allows some flexibility.

It is important, no matter what storage system is chosen, to keep it simple. Again, available resources will dictate what is feasible; of prime importance is to have a system that will work efficiently within the framework of the excavation.

In very general terms, if iron is found in a wet environment, then it should be kept wet. If dry, it should be kept very dry - 20-30% RH[10]. It is the in-between conditions: damp, wet/dry - that cause a bit of uncertainty. The method chosen for storage should be compatible with the planned conservation treatment. If an aqueous treatment method is going to be used, then iron should be kept wet: if porous corrosion layers dry out, they are extremely difficult to re-wet[11]. If the corrosion products will chemically alter to a state making future stabilization difficult, or physically damage the objects on drying, then the objects must be kept wet. In the case of composite objects (consisting of iron and other materials), storage must be selected that will not adversely affect the components.

Not every archaeologist and conservator has the luxury of being able to ship an entire collection back to a central conservation laboratory for treatment. The field storage system must be versatile enough to allow for easy separation of objects singled out for specific destinations and/ or treatments. In cases where objects cannot be removed from the country of excavation for treatment, then the storage system devised in the field must complement the resources of the organization that will be taking over responsibility of the material.

It can be seen that managing the conservation of a collection of archaeological material has many facets. The important point is that a plan must be established in order to avoid loss of information, loss of objects, and eventual chaos and attrition of material.

APPLICATION OF A PLAN

The Archaeology Division of the Canadian Conservation Institute (CCI) routinely gives advice to field archaeologists and curators of archaeological material on how to establish field handling, treatment and maintenance programmes. One of the most extensive and comprehensive projects that CCI has been involved in has been the excavation of a 16th century Basque whaling station at Red Bay, Labrador[12]. This project has involved cooperation among archaeologists, conservators and conservation scientists. As conservators, we feel that it serves as a good example of how planning for conservation from the early stages of excavation enabled the handling of large quantities of highly degraded and unstable, yet diagnostic material, to yield the maximum amount of information for both the archaeologist and conservator.

The Site at Red Bay

Traces of 16th century Basque structures were first found on beaches in the vicinity of Red Bay, Labrador, in 1977, during a survey under the direction of Dr. James A. Tuck of Memorial University of Newfoundland[13,14]. During preliminary excavations in 1978, Dr. Tuck requested conservation assistance from the Canadian Conservation Institute, and within a couple of days, a conservator (Ann Howatt-Krahn) from the CCI's Archaeology Division was on the site in order to do an evaluation of the conservation needs. She brought back samples of material and over the following winter, a plan was formulated on how to best handle the problem, given the constraints that:

1) CCI is not equipped to handle large volumes of material from any one site.

2) The iron was highly mineralized, very unstable and unresponsive to simple hot-washing techniques.

3) In the terms of Dr. Tuck's permit to excavate, issued by the Province of Newfoundland, he is required to turn over the material to the province in a "conserved condition".

4) There were no conservation facilities, or conservators, in Newfoundland.

From 1978 to 1983, Dr. Tuck has been excavating the Red Bay site with financial assistance from the Social Sciences and Humanities Research Council of Canada, the Province of Newfoundland, and with conservation assistance from the CCI.

Developing an Archaeology/Conservation Plan

Given the fact that CCI could not treat all the material at our Ottawa laboratory, and that the main conservation problem appeared to be handling large quantities of unstable material, a plan was devised that considered groups of materials rather than individual objects. Objects requiring specialized skills, equipment or analysis would be returned to CCI for treatment, but the bulk of material would be recorded and packaged then sent to Memorial where Tuck could provide storage facilities pending treatment.

The two main problem groups of material were waterlogged wood and iron[15]. The iron posed difficulties both in terms of recording and stabilization.

The objects were so highly mineralized that identification was often impossible. Another major problem was that no satisfactory conservation method existed for iron in this particular condition. The decision to x-ray the entire collection in the field was taken in 1979 in order to record condition of the objects, to assist in identification and to provide a permanent record of the objects since we couldn't guarantee that a conservation treatment would be 100% effective for all the material.

The need to keep the iron wet became obvious as dry samples began to disintegrate within a few months. After noting its instability in a dry, untreated condition, the decision was made to keep it wet until conservation was completed. On excavation, it is immediately put into buckets of fresh water. During cataloguing, objects are kept in shallow trays, covered with wet rags. Following cataloguing, conservation condition reports are done for each object, then the objects are individually wrapped in cotton gauze, tagged with an embossed Teflon tag and stored in fresh water, according to provenience. When enough objects from each area of the site have accumulated, they are secured in sandwiches of polypropylene screening made to the same size as two, 14" x 17" (35.5 cm x 43.2 cm) x-ray sheets, and the objects are then x-rayed. Tracings are then done of each radiograph and the catalogue number of the objects recorded on each tracing. The number of the x-ray that an object appears on is then recorded on the condition report for that object. The objects remain in their polypropylene sandwiches during shipping and in storage at Memorial. By this packing and recording technique, order is maintained and the archaeologist has a visual record of all the material from specific locations of the site even if the material is not easily accessible.

To date, the iron has been kept in 1% (w/v) NaOH solution for long-term storage. NaOH was chosen as the long-term holding solution for three reasons: (1) since the objects are found in a relatively saline environment, it seemed logical that chloride ions were playing a major role in the instability;

we were hoping that diffusion of chloride ions out of the corrosion layers would be more favoured in NaOH than deionized water[16]; (2) any metallic iron in the objects would be protected; (3) the objects were covered with a thick layer of humic material mixed with corrosion; this softens considerably in NaOH and facilitates mechanical cleaning of extraneous accretions.

The problem of how to eventually treat the objects was considered while devising a system for recording and storage. The mechanism of the rapid and quite spectacular disintegration of the objects had to be defined.

Dr. James Argo, while doing analysis of iron corrosion products for CCI's Analytical Research Services Division, identified three iron oxyhydroxides on dry, untreated Red Bay iron: goethite, lepidocrocite and akaganeite. The formation of akaganeite relies on the presence of chloride ions[17,18]. Argo identified akaganeite as being present in areas of active corrosion, and as being responsible for the rapid spalling and splitting observed on both the untreated and hot-washed Red Bay iron.

We had been preventing the formation of akaganeite on the Red Bay iron by keeping the objects wet since excavation. The problem was to devise an aqueous treatment that would extract chloride ions to a level that would preclude akaganeite formation. Ideally the treatment would not involve complex equipment or techniques, since the bulk of the iron would have to be treated by archaeology students at Memorial University in St. John's, Newfoundland.

Argo had been conducting experiments on the reaction of amines with iron oxyhydroxides[19]. He found that in aqueous solution, ethylenediamine (EN) has a pH of between 12-13, is positively charged and complexes chloride ions strongly. Iron oxyhydroxides are negatively charged at a pH of over 8.5[20]. It seemed possible that EN might be able to penetrate the corrosion layers and remove chloride ions from the corrosion cycle.

By testing for over two years at CCI, we found that it was possible to stabilize the bulk of the iron by heating in aqueous 5% (v/v) EN until chloride concentration reaches less than 20 ppm. We consider this treatment still to be in a developmental stage, with many questions yet to be answered about the specific mechanisms of the EN/corrosion/chloride ion interactions. However, since the treatment appears to be effective for the Red Bay material, we have decided to treat the highly mineralized objects with this technique.

Bulk treatment of the iron has begun at Memorial, using ethylenediamine immersion. CCI is monitoring the treatment solutions for chloride concentration. The final phase of the conservation of this iron, which began with careful handling in the field, is correct storage: a dry storage cabinet has been constructed at Memorial for all the treated metal from the site.

CONCLUSION

The conservation of large quantities of archaeological material is largely a management problem. Success of a conservation plan relies on cooperation between the conservator and archaeologist.

Advice from conservators should be sought at an early stage of excavation; conservators dealing with archaeological material must be familiar with and sympathetic to the constraints under which archaeologists are working.

Iron presents a special case, not just because of problems with its inherent instability, but also because it is often not adequately considered in terms of a total archaeology/conservation plan.

This paper has outlined some of the concepts involved in such a plan, and given an example of a cooperative effort in which the conservation of the iron, beginning in the field, has played a major role.

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INFRARED SPECTROSCOPY: A SUITABLE TOOL FOR THE CHARACTERIZATION OF COMPONENTS IN BRONZE PATINAS

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SUMMARY

The characterization of complex mixtures of compounds accumulating at the interface between metal and environment of bronze artifacts - especially if these consist of outdoor statues - is often difficult. Nonetheless it constitutes an important starting point for the conservator of metal objects who, following modern philosophy, must preserve all those components of the patina which are not dangerous for the statue.
This demands characterization of components of a patina and a knowledge of their chemical and physical properties in order to discover methods for their conservation or removal.
Many alteration compounds have polyatomic anions and water of hydration in their composition, both of which possess characteristic absorption bands in the infrared region.
In this paper, many single compounds are considered and their spectra are discussed (Corrosion products: basic sulphates, chlorides, nitrates, oxalates, carbonates of copper. Deposits of atmospheric pollutants: sulphates, nitrates, oxalates, carbonates, principally as calcium salts). In most cases characteristic sharp reproducible absorption peaks either permit direct identification or supplement diffractometric data to resolve specific analytical problems.

INTRODUCTION

The surface of bronze antiquities which are exposed outdoors shows nowadays a typically non-homogeneous appearance which directly testifies the presence of a complex variety of different solid species on it.
Some different kinds of processes may cause the progressive accumulation of a lot of extraneous products which both physically and chromatically modify the object.
The chemical oxidation of the metal alloy costitutes undoubtedly one of the first steps.
Oxygen and other oxidizing atmospheric pollutants (SO_x, NO_x) are the most prominent agents determining such initial stage of transformation.
In other cases, especially when two metals of different nature are in contact, a pile between them may be established which originates electrochemical processes (i.e. gilden bronzes etc.).
With the primary products formed in this way, other natural or polluting agents may further react, determining the rising of new solid phases.
These subsequent transformations are principally due to hydrolysis, "double-change", salification and other chemical reactions.

In this way for example, carbonates may be changed into sulphates; oxides into sulphides; sulphates into oxalates etc.
Another more properly physical phenomenon consists in a continuous deposit and accumulation of atmospheric solid particulates on the surface.
Among them, both soluble and insoluble compounds may be found. The first may cause some of the above mentioned secondary chemical transformations; the others (silicates, carbonates, carbon, quartz etc.) contribute to the formation of thick greyish and unaesthetic incrustations.
Finally, we must not undervalue the presence of a lot of organic materials introduced during some previous restorations: waxes, oils, resins etc.
This remarkably complex situation makes indispensable the employment of more than one analytical approach. X.R. diffractometry and I.R. spectrophotometry distinguish themselves as the most suitable and appropriate techniques.
In this paper the latter is specifically considered through the presentation of a series of I.R. reference spectrograms of typical products which more commonly may be found in the patinas of outdoor bronzes.
I.R. spectrophotometry gives in most cases characteristic analytical "finger prints" which decisively facilitate the identification of a single degradation compound.
The characterization of patinas constitutes indeed the first absolutely necessary step in the conservation of bronze artifacts.
This knowledge is particularly important in this sector more than others, where the lacking of a precise and competent philosophy of conservation is deeply perceived.

EXPERIMENTAL

Infrared absorption spectra of reference standard compounds were recorded on a Perkin Elmer Model 157G Spectrophotometer operating in the region $2.5 \div 16\mu$ (wavelength), 4000-625 cm^{-1} (wavenumber).
It is a simple instrument which may be found in many laboratories; nevertheless it resulted more than appropriate for a good characterization of the considered compounds.
Samples were dispersed utilizing the tecnique of KBr disc (1.5-2mg of sample in 100mg of KBr).
In about half an hour it is possible to obtain an I.R. absorption spectrum to compare, more conveniently as a "finger print", with reference standard spectra.
The following classes of compounds were considered:
copper salts (corrosion) (chlorides-sulphates -nitrates-carbonates-oxalates)
calcium salts (deposit) (sulphates, nitrates, oxalates, carbonates)
Quartz and silicates (deposit)
degradation Lead products (corrosion) (sulphate)

When commercial products were available, analytical grade reagents were used. In other cases mineral samples were employed. When both resulted irrecoverable, standard compounds were artificially prepared through a chemical synthesis followed by diffractometric checking of the identity. In such cases the procedure adopted for the synthesis is reported.
Many reactions which are referred to in the bibliography were found to give only mixtures of basic salts.

COPPER CHLORIDES

Four cupric neutral and basic salts were examined.

$Cu_2(OH)_3Cl$ ATACAMITE   blue-green rhombic pyramidal

$Cu_2(OH)_3Cl$ PARATACAMITE   light blue-green trigonal

$Cu_2(OH)_3Cl$ BOTALLACKITE   blue green monoclinic prismatic

$CuCl_2 \cdot 2H_2O$ ERIOCHALCITE   light blue green - rhombic

In figs.1a,1b significant partial region of relative I.R. spectra are reported.
The following samples were utilised:

Eriochalcite - Merck, cupric dihydrated chloride.

Paratacamite - synthetic product obtained from metallic copper in foil, suspended in a dilute solution of cupric chloride under stirring for a few days (1).

Botallackite - synthetic product: cupric chloride (1g in 4cc of water) + cupric oxide powder (10mg) maintained a week at 110°C in a soldered vial (2)

Atacamite - synthetic product obtained from calcium carbonate + water solution of cupric chloride, being continuously stirred for a few days.

In the following table the wavenumbers corresponding to characteristic absorption peaks and bands are reported (vs = very strong; s = strong; m = medium; w = weak; br = broad).

Atacam.	Paratac.	Botall.	Eriochal.
		3520 vs	
3440 s	3440 vs	3435 vs	
3335 vs	3350 vs	3350 vs	
	3310 vs		3320 vs/br
			3260 vs
			3170 vs
			1605 s
985 s	985 s		significant bands are absent in this region.
945 s			
915 m	920 s		
890 s	905 w	870 m	
845 s	860 s	855 s	
820 w	825 s	820 s	
		785 vs	
		700 vs	

SULPHATES

The following salts of Copper, Calcium and Lead were considered:

$Cu_3(OH)_4SO_4$ ANTLERITE   - green - rhombic bipyramidal

$Cu_4(OH)_6SO_4$ BROCHANTITE   - light blue green monoclinic prismatic

$CuSO_4 \cdot 5H_2O$ CHALCANTHITE   - blue - triclinic

$CaSO_4 \cdot 2H_2O$ GYPSUM   - white - monoclinic prismatic

$CaSO_4$ ANYDRITE   - white - rhombic bipyramidal

$PbSO_4$ ANGLESITE   - white - rhombic bipyramidal
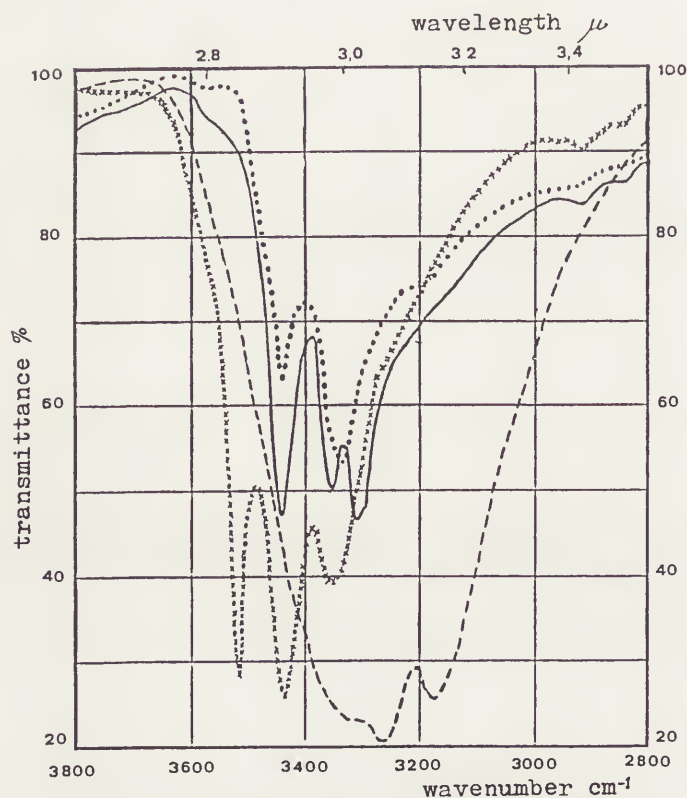
Fig.1a - Infrared absorption spectra of cupric chlorides in the region 3800-2800 cm^{-1}

——— Paratacamite $Cu_2(OH)_3Cl$

----- Eriochalcite $CuCl_2 \cdot 2H_2O$
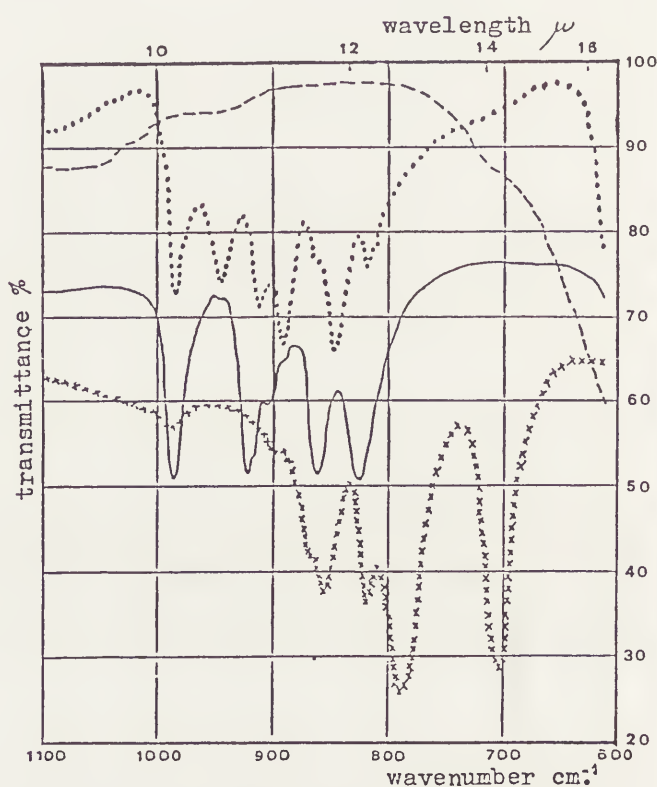
Fig.1b - Infrared absorption spectra of cupric chlorides in the region 1100-625 cm^{-1}

····· Botallackite $Cu_2(OH)_3Cl$

······ Atacamite $Cu_2(OH)_3Cl$

The spectra of Chalcanthite, Gypsum and Angle-site were recorded utilizing samples of corresponding Merck analytical reagents.
Anydrite was prepared by dehydration of gypsum at 200°C for three hours.
Antlerite was synthetically obtained starting from $CuSO_4.5H_2O$ (1g in 5cc of water) + cupric oxide powder (.2g) maintained a week at 110°C in a soldered vial.

Brochantite was easily prepared adding d.by d. a water solution of NaOH (.2g in 10cc of water) to a water solution of $CuSO_4.5H_2O$ (3.3g in 40cc of water).
The relative partial spectra are shown in figures 2a, 2b.
Infrared absorption bands are tabulated (wavenumbers) below:

Antlerite	Brochantite	Chalcanthite	Gypsum	Anhydrite	Anglesite
	3585 s	a broad not significant band is present			
3570 vs	3560 s		3550 vs	significant bands are absent	significant bands are absent
3485 vs					
	3390 vs		3410 vs		
	3280 s				
			1685 w		
			1680 m		
		1200 vs			
1150 s		1160 vs	1145 vs / 1110 br	1150 vs / 1100 br	1160 s,br
1105 vs	1120 vs				
1075 s	1090 vs	1085 m			
					1050 vs,br
985 w	980 m	995 vs			
		960 s			965 m
	940 m				
885 s	875 s				
850 m	850 s				
800 m	780 m				
755 m					
	730 m				
660 w		655 vs	665 s	675 s	
635 s	625 m				630 s
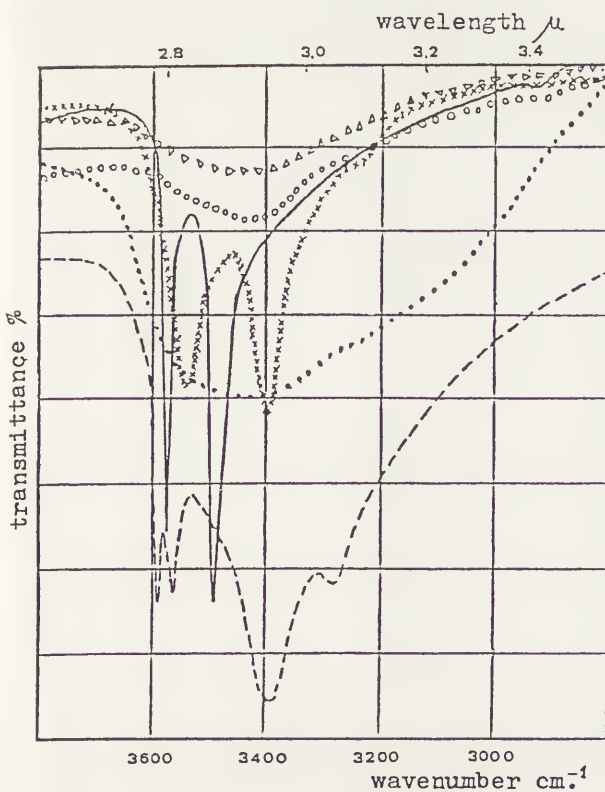
Fig.2a – Infrared absorption spectra of cupric and calcium sulphates in the region 3800-2800 cm⁻¹

———— Antlerite $Cu_3(OH)_4SO_4$
----- Brochantite $Cu_4(OH)_6SO_4$
······· Chalcanthite $CuSO_4.5H_2O$
ˣˣˣˣˣ Gypsum $CaSO_4.2H_2O$
ₒₒₒₒₒ Anglesite $PbSO_4$
ᴬᴬᴬᴬᴬ Anidrite $CaSO_4$
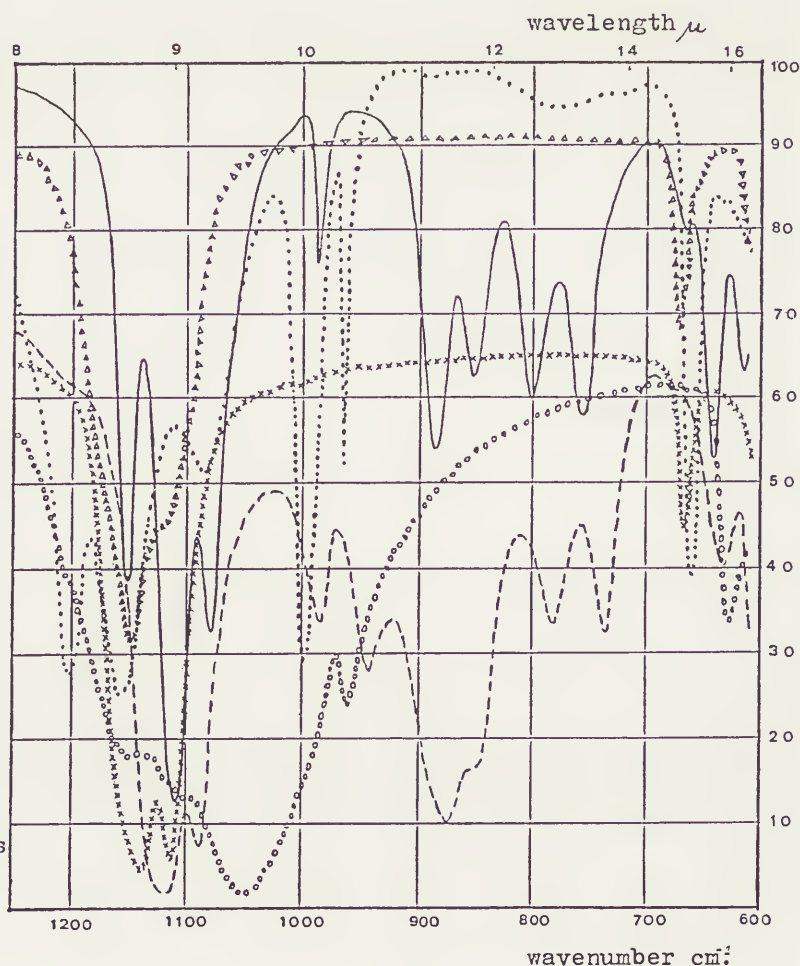
Fig.2b – Infrared absorption spectra of cupric and calcium sulphates in the region 1250-600 cm⁻¹

NITRATES

Two Copper and one Calcium salts were considered.

$Cu(NO_3)_2 \cdot 3H_2O$ trihydrate cupric nitrate - blue

$Cu(OH)_3NO_3$ basic cupric nitrate - blue green

$Ca(NO_3)_2 \cdot 4H_2O$ tetrahydrate calcium nitrate - colourless

Samples of $Cu(NO_3)_2 \cdot 3H_2O$ and $Ca(NO_3)_2 \cdot 4H_2O$ consisted of Merck analytical reagents. $Cu_2(OH)_3NO_3$ was synthetically obtained from cupric oxide (.4g) + $Cu(NO_3)_2 \cdot 3H_2O$ (1.2g) in 2cc of water maintained for a week at 110°C in a soldered vial (2).

The relative absorption spectra are shown in figs.3a,3b and tabulated (wavenumbers) below:

$Cu(NO_3)_2 \cdot 3H_2O$	$Cu_2(OH)_3NO_3$	$Ca(NO_3)_2 \cdot 4H_2O$
	3530 s	
	3420 s,br	3450 vs,br
3320 vs,br		
3260 vs		
3170 vs		
		2425 v w
2390 w		
1765 w		
		1630 m,br
1605 vs,br		
	1415 vs	1430 s,br
1390 vs,br	1380 vs	1385 vs
	1335 vs,br	1355 m
	1045 m	1045 w
	870 m,br	
825 m		820 w
	805 w	
	770 m,br	
	665 m,br	
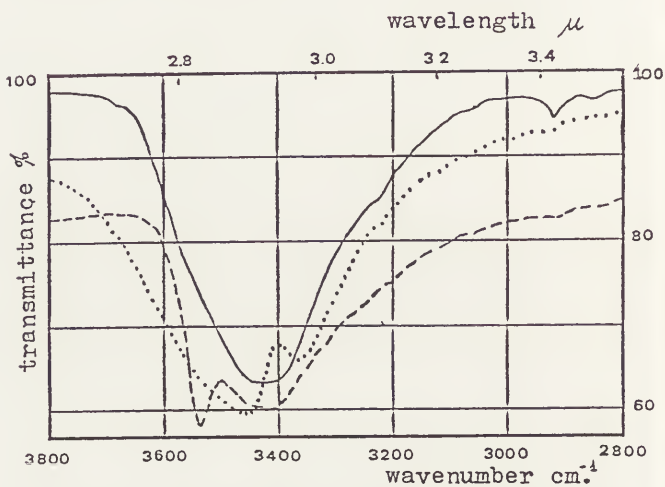
Fig.3a – Infrared absorption spectra of copper and calcium nitrates in the region 3800–2800 cm.⁻¹

—— Calcium nitrate $Ca(NO_3)_2 \cdot 4H_2O$

----- Cupric basic nitrate $Cu_2(OH)_3NO_3$

········· Cupric nitrate $Cu(NO_3)_2 \cdot 3H_2O$
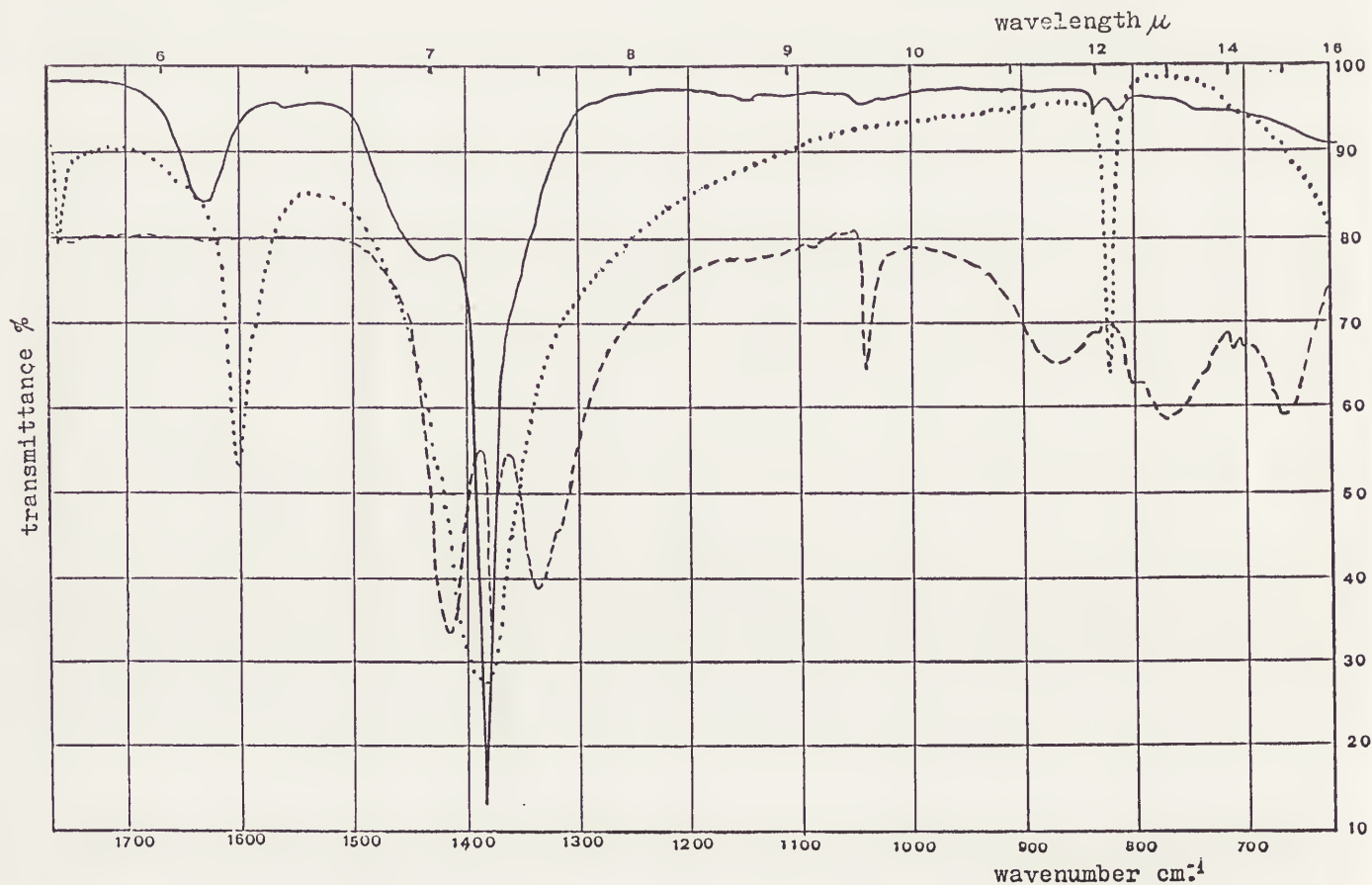
Fig.3b – Infrared absorption spectra of copper and calcium nitrates in the region 1770–625 cm⁻¹

—— Calcium nitrate $Ca(NO_3)_2 \cdot 4H_2O$

----- Cupric basic nitrate $Cu_2(OH)_3NO_3$

········· Cupric nitrate $Cu(NO_3)_2 \cdot 3H_2O$

CARBONATES

The following Copper and Calcium salts were examined:

$Cu_3(OH)_2(CO_3)_2$ AZURITE – blue – monoclinic prismatic

$Cu_2(OH)_2CO_3$ MALACHITE – green – monoclinic prismatic

$CaCO_3$ CALCITE – white-trigonal

$CaCO_3$ ARAGONITE – white – rhombic bipyramidal

The corresponding mineral-pure samples were employed in all four cases.
The relative spectra are reported in figs. 4a, 4b and in the following table.

Azurite	Malachite	Calcite	Aragonite
3425 s	3410 s		
	3320 s		
		2880 w br	
		2510 w	
		1800 w	1780 w
1490 s	1500 vs		
1465 m			
1415 vs	1425 s	1430 vs,br	1470 vs,br
	1390 vs		
1090 m,br	1095 m		1080 w
1030 m-s,br	1050 vs		
950 m-s			
	880 s	875 vs	
			850 vs
835 m	820 s		
795 m			
770 m	750 m		
	710 w	710 w	710 m
695 w			690 w
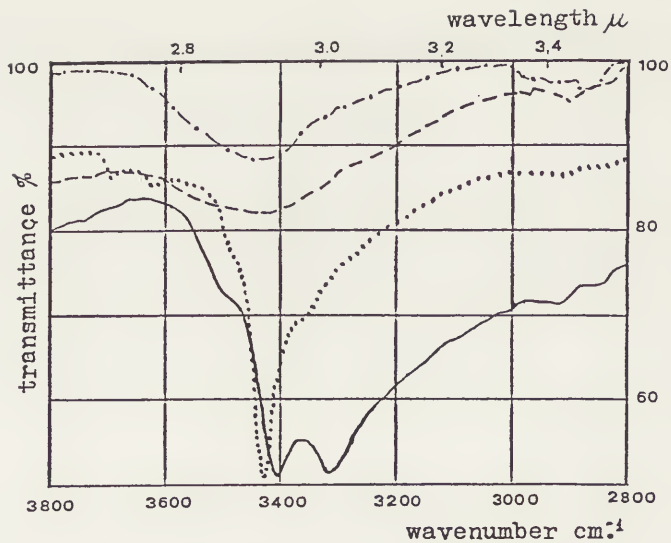
Fig.4a – Infrared absorption spectra of Calcium and Copper carbonates in the region 3800–2800 cm^{-1}

·········	Azurite	$2CuCO_3.Cu(OH)_2$
————	Malachite	$CuCO_3.Cu(OH)_2$
–·–·–	Calcite	$CaCO_3$
– – – –	Aragonite	$CaCO_3$
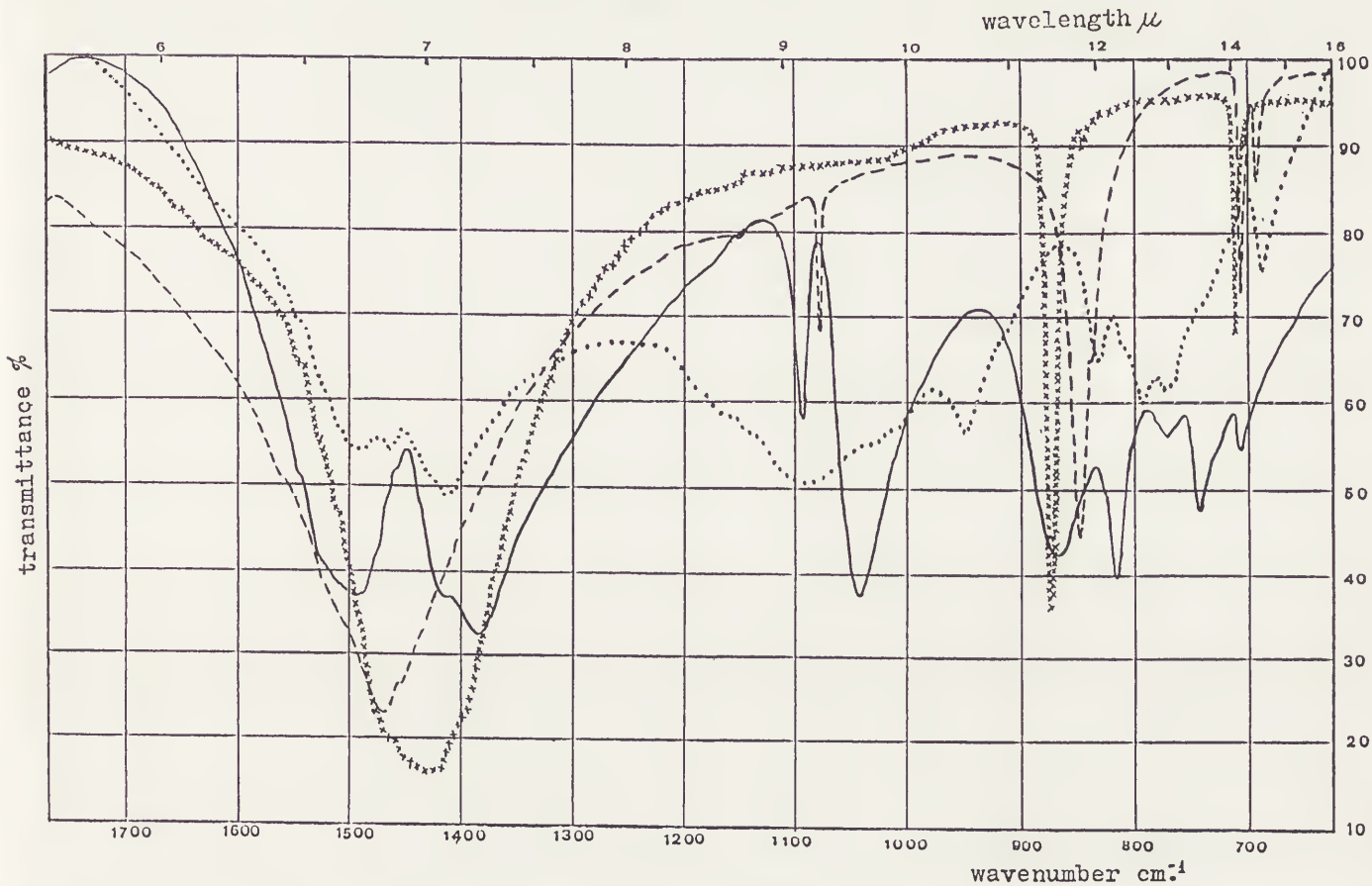
Fig.4b – Infrared absorption spectra of Calcium and Copper carbonates in the region 1770–625 cm^{-1}

·········	Azurite	$2CuCO_3.Cu(OH)_2$	××××××	Calcite	$CaCO_3$
————	Malachite	$CuCO_3.Cu(OH)_2$	– – – –	Aragonite	$CaCO_3$

OXALATES

Two salts of Calcium and one of Copper were considered:

$CuC_2O_4.n.H_2O$ – cupric oxalate – light blue green

$CaC_2O_4.H_2O$ – WHEWELLITE – white

$CaC_2O_4.2,5H_2O$ – WEDDELLITE

The copper oxalate was synthetically prepared from cupric basic carbonate (analytical Merck reagent) made to react with a water solution of oxalic acid (Merck).

Whewellite was pure calcium oxalate Merck.

Weddellite resulted not available as a mineral sample.
It was also impossible to obtain this crystalline calcium oxalate by synthesis.
The standard reference spectrum which is partially reported in fig.5b, was obtained utilizing a sample of a natural patina taken from a marble statue.
The sample resulted very rich of Weddellite by a X.R. diffractometry analysis.
In the table below the relative position of absorption peaks are reported.

$CuC_2O_4.nH_2O$	Whewellite	Weddellite
	3480 m	3480 m ?
	3430 m	?
3600–3300 m,br	3340 w	?
	3260 w	?
	3060 w,br	3060 w ?
1660 vs,br	1625 vs,br	1645 vs,br
1370 s	1385–70 w,br	?
1325 m	1320 s	1325 s
825 m		
	775 m	785 m
	665 w,br	

SILICATES

Infrared spectrometry is not the most suitable technique for the characterization of silicates. Nevertheless it is important to recognize the presence of such compounds as a class in the patinas.
Two spectra are reported (fig.6) and tabulated:
α Quartz (mineral sample), and a sandstone (Pietra serena) which frequently occur in atmospheric particulates of our country.

α-Quartz	Sand
3600–3400 w,br	3600–3400 w,br
1470–1400 w,br	1470–1400 w,br
	1070 vs,br
	1025 vs,br
	875 w
	795 m
	775 m
	695 w
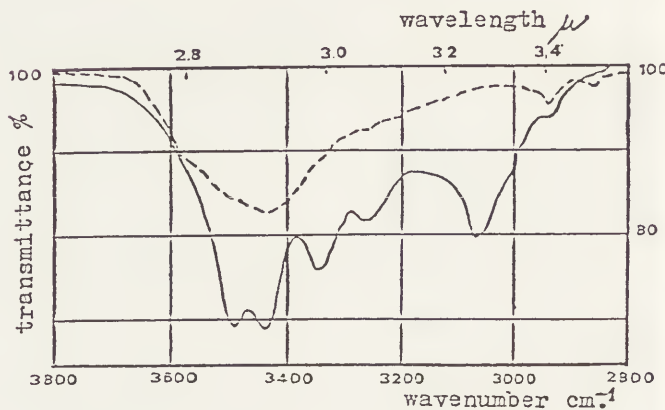
Fig.5a – Infrared absorption spectra of Calcium and Copper oxalates in the region 3800–2800 cm⁻¹

—— Whewellite $CaC_2O_4.H_2O$

---- cupric oxalate $CuC_2O_4.nH_2O$
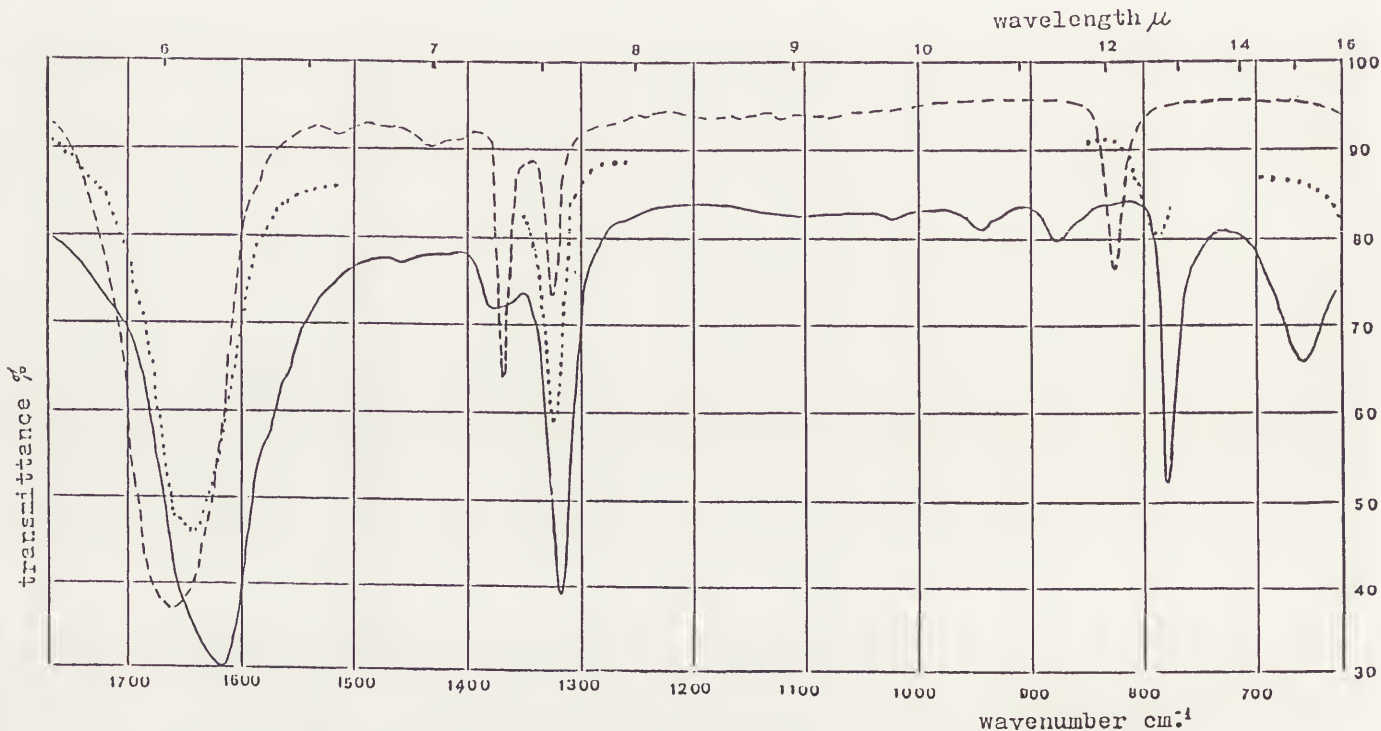
Fig.5b – Infrared absorption spectra of Calcium and Copper oxalates in the region 1750–625 cm⁻¹

—— Wewellite $CaC_2O_4.H_2O$ --- Cupric oxalate $CuC_2O_4.nH_2O$ ···· Weddellite $CaC_2O_4.2,25H_2O$
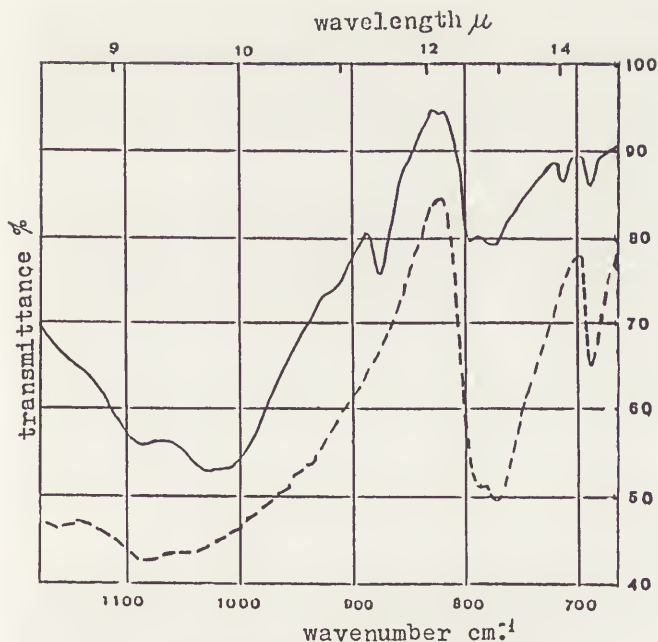
Fig.6 - Infrared absorption spectra
of silicates in the region
1180-670 cm^{-1}

---- α Quarz SiO$_2$

——— sandstone "Pietra serena"

DISCUSSION

The reference spectra that here are considered can be conveniently grouped depending on the type of anion present in the salt. A strong I.R. absorption band is indeed associated with the bands, in the poliatomic anions. Such broad and very strong bands are almost always characteristic of an anion:

sulphates in the region 1240-970 cm^{-1} vs/br
carbonates " " " 1550-1300 " vs/br
oxalates " " " 1720-1550 " vs/br
silicates " " " 1200-900 " vs/br
nitrates " " " 1450-1300 " vs/sharp

Chlorides, though lacking a poliatomic anion, may be recognized through a series of absorption peaks or bands associated to water coordination molecules or to the presence of hydroxil groups.
They are not characterized therefore as a class but as single compounds.
For the others, once the type of anion is identified, one can proceed to the attribution of the spectrum to a specific compound through the assignment of the other peaks, (associated with H$_2$O, OH as well as with the anion).
An exhaustive systematic analysis of every single peak would result a much too complicated procedure. The method of comparison with reference spectra constitutes undoubtedly the most simple and successful approach.
CHLORIDES - They represent the most worrying corrosion products that can be found in the patina of bronzes. The well known "bronze disease" is indeed primarily related to the presence of copper chlorides and consists in a cyclic, self-feeding chemical process.
Basic copper chlorides are chiefly accumulated in close connection with red cuprous oxide (Cuprite).
Atacamite and Paratacamite are the most commonly found chlorides in our analytical experience. Their I.R. spectra are rich of differentiating elements.

SULPHATES - Owing to the continuously increasing atmospheric pollution, sulphates represent nowadays the most common degradation compounds in bronze antiquities.
Sulphates green patinas took the place of antique carbonatic films. But, while the latter constituted a coherent and protective layer on the metal, sulphates, being partially soluble compounds, determine a non-homogeneous coating which is no more protective.
Also the colour may be changed due to the presence of grey external concretion made of Gypsum and carbonaceous particulates.
Gypsum, Brochantite and Antlerite are the most frequently identified sulphates.
Chalcanthite is less commonly found probably because it is washed away being a water soluble salt.
NITRATES - They may result either from atmospheric pollution or from decomposition processes of proteinaceous biological material. In some cases previous cleaning operations carried out by nitric acid may have also determined the formation of nitrates. The basic cupric nitrate which is reported was effectively identified on the gilden bronze doors of the Baptistery in Florence (3).
CARBONATES - As it was already referred with regard to sulphates the recognition of copper carbonates on outdoor bronze antiquities is a decidely rare opportunity. More frequently they can be found in archeological artifacts. Calcium carbonate, on the other hand, is frequently found as a deposit on bronze fountains.
OXALATES - These salts, which are less known and reported than others, are however very frequently present in the green patinas of outdoors works of art. They occur both as Copper and Calcium salts but their origin is still obscure and uncertain. Spectrum of Weddellite is incompletely reported. Absorption bands at 1645,1325,785 cm^{-1} are surely belonging to it. In the other region we reasonably believe that no further significant absorption occurs.
SILICATES - They are characteristic diffuse deposit-compounds originated from atmospheric solid pollutants.
Every country possesses its typical atmospheric particulates. Hence, we have reported only those which are frequent in our region: Quartz and a particular sandstone.

CONCLUSION

The I.R. spectra that here are reported and tabulated don't obviously represent the complete list of all the possible compounds which may be found in the patina of a bronze artifact. Nonetheless they constitute a basic budget of reference materials that here are collected and usefully subdivided into different chemical families to facilitate any comparative study or analysis.
In many cases spectra are reported which are very difficult to find or are completely absent in the specific bibliography.

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Current Research into the Corrosion of Archaeological Iron

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Summary:

In the late nineteen seventies it seemed apparent to scientists and conservators at the Canadian Conservation Institute and elsewhere, that very little real progress had been made in the preceeding years to understand the problems of treating corroded archaeological iron. We felt that because of our involvement with the excavation at Red Bay, Labrador, we had the expertise, an ideal situation and a legitimate need to become involved in this field ourselves. In 1980 we began a programme of research to address some of the problems we were faced with at that time.

This paper provides an overview of how that programme has been organized, and what is presently being investigated. Some of the projects briefly described are: (1) an evaluation of holding solutions and (2) de-oxygenated conditions for the long term storage of iron, (3) the characterization of iron artifacts from immediate post-excavation to post-treatment; and, (4) continuing work on the use of ethylenedia- mine in treating highly mineralized iron.

The intention is not to report results, but to make others aware of what is being done, and to solicit their comment and input.

Introduction:

The preservation of archaeological iron has been one of the most difficult aspects of conservation in the past and continues to be so today. It has been known for a long time that chlorides attack iron. As early as 1882, Krause identified the yellowish/green beads of liquid he saw forming on corroding iron artifacts, as being solutions of ferrous chloride (1). He further described the formation of "oxyhydroxides" via basic ferrous chloride intermediates. As a result of these and other studies it was concluded that the presence of chlorides greatly accelerated the corrosion of iron and that their subsequent removal was essential for the preservation of archaeological iron artifacts.

Since this time numerous methods have been advanced describing the extraction of chloride salts from iron artifacts. In recent years, the more commonly used conservation methods to stabilize iron artifacts to further corrosion has produced many unpredictable results, which has drawn considerable attention to the subject. Until relatively recently a rather haphazard approach has generally been taken in an effort to find a practical and efficient solution to the problem. This has occasionally resulted in measures being recommended and implemented without serious consideration of their effectiveness or consequences.

Given that the presence of chloride ions is the major factor in promoting further corrosion and that their removal is essential to the stabili-zation of iron artifacts, it would seem that the most important point to be considered is the exact nature and context of the chloride in the corroded iron artifact. Failure to establish this before developing or applying conservation methods has resulted in some ineffective treatment methods and considerable confusion.

There was a need to approach problems in a logical fashion and to develop treatment methods from a foundation of meaningful facts rather than intuition. It was at this point in time, 1980, that the Canadian Conservation Institute (CCI) decided to expend some of its research effort looking into some of the problems then prevelent in iron conservation. With our involvement in the excavations at Red Bay, Labrador as impetus, we began by undertaking a programme of analysis to identify the precise nature of the corrosion products on iron from marine sites (2).

Development of a Research Programme:

The CCI is quite a large organization which offers an opportunity for scientists and conservators to work closely together on a wide range of problems. For the first two years of our involvement with iron research one scientist was assigned to the problem. However, in 1982, convinced of the wisdom of encouraging scientists and conservators to work together, an iron corrosion research team (ICRT) was formed under my general direction. Today, four scientists and three conservators collaborate on the planning, execution and interpretation of various problems which had been identified by the group as being of importance and within our area of expertise and interest. Each specific problem/ project is assigned to a smaller working group that meets frequently and is responsible for day-to-day practical decisions. The working group is comprised of the principal researcher and others who can provide significant input. In all cases this includes a representative of the Analytical Research Services Division of CCI, which plays a significant role in the programme and provides the analytical support essential to these projects. The ICRT meets less frequently and is essentially a forum for discussion, major decision making and project review.

Whilst the ICRT was formed as a suitable way to manage iron research activities at CCI, it was also seen as an appropriate vehicle for formalizing the already existing exchange of ideas, information and assistance between CCI and the Conservation Division of Parks Canada. This conservation facility lies less than one mile distant from CCI and is comprised of conservators and scientists charged with the conservation and study of artifacts from Canada's designated historic parks and sites. Over the past several years a very large number of these artifacts have been archaeological iron.

In close proximity were two institutions involved with iron conservation. One (Parks Canada), having to treat large quantities of iron on a routine basis, and one (CCI) strongly mandated to carry out conservation research and actively involved with iron conservation problems. The benefits of collaboration were obvious and a conservator and conservation scientist from Parks Canada are members of the ICRT. Resources and expertise from both organizations are freely applied to common problems.

From its early meetings the team identified various projects to be undertaken. Brief outlines of those being carried out at CCI are given below.

It has been apparent for some years that the post-excavation treatment of iron artifacts is of paramount importance. Artifacts from both marine or wet land sites if allowed to dry out in an uncontrolled fashion, can exfoliate, delaminate, crack and corrode actively. To prevent this there

would appear to be a limited number of options: store the objects "dry", below the critical humidity of 20% cited by Turgoose (3); freeze the artifacts, thereby slowing down all processes and preventing migration of water; or, keeping the objects wet until a stabilizing process can be undertaken. It was decided to evaluate wet storage methods.

A. EVALUATION OF CONVENTIONAL HOLDING SOLUTIONS:

The idea is that one prevents excessive physical damage to the artifact by keeping it wet and, at the same time, removes chloride ions. It is also believed that the solutions inhibit further corrosion. In practice, however, unwanted physical and chemical changes may take place on the artifact if stored for long periods, which can interfere with subsequent conservation processes. It was to investigate such ideas in a systematic fashion that this project was undertaken.

Six different holding solutions are being evaluated at room temperature. These are: 1% W/V sodium hydroxide; de-ionized water; 2% V/V ethylene-diamine; alkaline-sulphite (0.5M); 1% W/V sodium carbonate; and, synthetic seawater. Two groups of artifacts are being stored in these solutions, wrought iron nails from a seawater site in the Gaspé, Québec; and nails from a wet land site at Red Bay. Each solution also contains a piece of polished pure iron as a control to measure the rate of corrosion. The solutions are being monitored at regular intervals for the following:

1. Dissolved oxygen: a YSI dissolved oxygen probe and meter is used to measure the dissolved oxygen content of the slightly stirred solution.

2. Chloride concentration: atomic absorption spectrophotometry (AA) is used to measure silver left in solution after precipitating out silver chloride. This method tends to be more accurate for high rather than low concentrations of chloride. However, analysis of standards has given consistently accurate results.

3. Iron concentration: a representative sample of solution and precipitate is taken from the stirred storage solution. This is then acidified with nitric acid (17%) and analysed using AA.

4. Calcium: calcium and iron are determined from the same acidified solution. To prevent masking of calcium by ethylenediamine a solution of strontium nitrate (300 ppm) is added to all samples before analysis by AA.

5. Sulphates: sulphates in solution are measured by first adding barium chloride (200 mg/ml.) to precipitate out barium sulphate, and then measuring the barium remaining in solution using AA.

Analysis for sulphate is obviously impossible with the alkaline-sulphite and synthetic seawater solutions. This latter solution is not monitored for calcium and chloride.

Solutions are monitored weekly and changed every 2 to 3 months. At the end of the experiments the artifacts will be sampled for characterization and then treated by various methods. It is hoped that in approximately one year this project will have revealed some of the consequences of using the above holding solutions and provide sufficient information to make logical choices of which solution or conditions are best suited to a particular problem.

B. STORAGE UNDER DE-OXYGENATED CONDITIONS:

Removal of oxygen from the storage solution should approximate the essentially anaerobic conditions of most burial sites and prevent further corrosion of the metal core and oxidation of the ferrous ions in the corrosion layers. This should prevent the formation of corrosion products which would interfere with the diffusion of the chloride through the corrosion layer into the wash water. In addition, such solutions with a tendancy towards a neutral pH should be more suitable for the storage of composite materials.

Three oxygen scavengers (ascorbic acid, sodium sulphite and hydrazine) were chosen after evaluating the literature. These are being tested together with two standards - de-ionized water and de-ionized water purged continuously with nitrogen. Each test solution contains three cannonballs excavated from a marine site, and a piece of polished pure iron to measure the rate of corrosion. The solutions are tested monthly for dissolved oxygen content, pH and chloride ion concentration. At the time of writing the experiment has been running approximately six months. Sodium sulphite has given the best results - the oxygen content has remained very low, the pH has stayed close to neutral, and the solution is clear. The cannonballs have taken on a pleasing blue-black colouration. Experiments will continue for a further six months.

C. THE CHARACTERIZATION OF CORRODED ARCHAEOLOGICAL IRON:

To be able to develop successful processes to solve particular conservation problems and evaluate the outcome of those processes, it is essential to characterize the artifact, both before and after treatment.

In a similar way, it has been sensibly argued (4) that one must be aware of any changes that take place on an artifact, especially in that period between excavation and subsequent treatment and stabilization. To this end, a characterization programme is being implemented. Samples representative of the artifacts used for the projects described, and others to study the importance of on-site sampling and immediate post-excavation handling and storage, have been taken for analysis. This will include the following: x-radiography, total chloride analysis, scanning electron microscopy and x-ray energy spectroscopy for chloride distribution, identification of corrosion products and transformation products by x-ray diffraction, and metallographic examination.

The degree of mineralization, porosity of corrosion layers, chloride distribution, nature of chloride, absolute quantity of chloride and environment of chloride will determine by what means and how successfully an artifact can be treated. For example, chloride at or near the metal surface will be more difficult to remove than that situated at the outer layers of corrosion product. It is hoped that the significance of these and other factors will be clarified by this programme.

D. FURTHER DEVELOPMENT OF THE AMINE PROCESS:

Since 1979, the CCI has been actively involved in the conservation of artifacts from the 16th century Basque whaling station at Red Bay, Labrador (5). The site from the outset, produced large quantities of highly mineralized, unstable waterlogged iron in the form of thousands of nails, fragments of hardware, whaling and cooping tools. Conservators found that this material posed many problems, particularly the lack of a really suitable conservation process for iron found in this condition. Initial experiments showed that hot water extraction was not effective in removing chlorides, and that the alkaline sulphite method (6) applied to a large batch of nails, previously stored in 1% sodium hydroxide, produced objects that were stable

but fragile.

The work to identify the corrosion products on marine iron had showed that akaganeite (β-FeOOH) was present on iron that had been allowed to dry out. Akaganeite, which is known to form by the damp oxidation of ferrous chloride tetrahydrate in contact with iron metal, has between 3-6% chloride incorporated into its crystal lattice structure. It can be transformed to stable magnetite under moist conditions and in the presence of iron metal, or can hydrolyse to goethite (α-FeOOH). Thus, under the right conditions, akaganeite can provide chloride ions which can promote renewed corrosion. It was decided to study the possibility of removing the chloride from akaganeite. James Argo experimented with ethylenediamine which forms stable salts with aqueous mineral acids, such as hydrochloric. In addition, from an experiment that exposed synthetic akaganeite to ethylenediamine vapour at the boiling point, there was evidence to suggest that akaganeite could be transformed to the stable magnetite (Fe_3O_4) using this reagent. These observations led to the development of a new conservation process for iron, the amine-process (7).

The method used presently involves immersing iron objects in a bath of ethylenediamine (5%) at 70°C. Chlorides are extracted into the bath. Chloride concentration is monitored and the baths are changed at regular intervals. A full treatment lasts a matter of months depending upon the mass of iron treated and its degree of mineralization. The sequence of hot baths is continued until chloride levels stabilize at a low level. Objects treated by the amine process appear to have an enhanced stability towards high RH, probably because residual amine acts as an inhibitor against corrosion.

This work is still in the development stages. More work is needed to understand exactly what happens in the process and how it can be optimized. Long-term testing programmes are being set up to test the stability of the treated artifacts and to evaluate the success/failure rate as related to artifact type and history, etc.

Other projects are in their formative stages or are anticipated. These include, attempts to model an active corrosion site and the application of thermal analysis to iron conservation problems. These projects are likely to be undertaken as collaborative efforts with the Physics Department of McGill University in Montréal.

Conclusion

In the late nineteen seventies the needs of conservators at the Canadian Conservation Institute for more effective and predictable treatment methods for corroded archaeological iron artifacts

led to the beginning of research to identify and try to solve the inadequacies of available conservation processes. Research into the nature of iron corrosion products and the use of ethylenediamine to stabilize iron began early in 1980. The inherent complexity and difficulties in treating this type of material became apparent during the course of this early work. A broader based approach involving the close collaboration of scientists and conservators has since been implemented.

The Iron Corrosion Research Team is in the process of investigating the effects of various holding solutions and de-oxygenated conditions for the long-term storage of iron. Analytical techniques are also being developed to characterize the condition of artifacts and to monitor the changes induced by conservation treatment.

The major purpose of this paper is to inform the Working Group of the work that we are doing and the approach that we are taking. We are trying to answer a number of different questions which we consider to be important. The work is still in its infancy, and we would welcome comment, criticism and input from others working in the field.

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ON GRADUAL REMOVING CORROSION LAYERS FROM METAL, STONE AND CERAMICS

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Summary

A method of removing carbonate and corrosion layers from the surface of objects made of metal, stone and ceramics with the help of film-forming solutions of polymer-polyelectrolites containing carboxyl groups has been proposed and successfully used in the State Hermitage. The application of these solutions makes it possible to remove the layers gradually and to clean the objects to the desirable degree.

Oxide and carbonate layers from the surface of objects made of metal, stone and ceramics are removed now by using methods which has long been known. Metal objects are either cleaned mechanically or submerged into a bath with the solutions of oxides and carbonates reacting substances. The former method is rather labour- consuming. When using the latter, it is difficult to control the extent to which the corrosion layers are removed. Special difficulties are experienced in cases when the metal surface is covered with a thin relief, partly damaged or subjected to exfoliation, as well as when the metal is combined with some other material (wood, leather, textile, bone,etc.).

To remove carbonate layers from works of art made of limestone, marble, alabaster, plaster of Paris, slightly baked ceramics requires much time as the carbonates must be carefully removed with a scalpel. The surface contaminations of objects made of stone and some other materials are removed with the help of some film-forming solutions of water-soluble polymers. This technique has been used in the Hermitage for already several years. The solution is put on the surface of the object and after the water evaporates the contaminations are removed together with the polymer film which absorbed them (I). Dense layers of considerable thickness (carbonate formations on stone or ceramics and the corrosion products of metal) cannot be removed by using this method. It could be assumed that applying polymers whose macrochains contain reactive groups with reference to the compounds mentioned would enable this process to be improved. That is why we tried and offered a method which consisted in putting on the surface to be cleaned some polyelectrolite solutions containing carboxylic groups (2). The corrosion and carbonate products are removed layer after layer which is achieved due to the fact that the reaction takes place only with the part of the compound which is in direct contact with the polymer carboxylic groups.

The electrolites must satisfy the following requirements:

I. The reaction must take place only with oxide or carbonate compounds.

2. The solution must be viscous, convenient to be put both on the horizontal and vertical surfaces.

3. The polyelectrolite film must be easily removed from the object it was put on.

In the Hermitage chemical laboratory some methods of the polyelectrolite synthesis fitting the above requirements were worked out. They are based on the use of the methacrylic acid and the styrene-maleic anhydride copolymer. The polymethacrilic acid was synthesized by a much simpler technique than the routine one. Its IO-I5% concentration water solutions have pH about 3 and that is why it cannot be recommended for removing the corrosion layers as it reacts with the non-oxidized metal. The pH increase up to 4,5 - 5,5 eliminates this reaction. To increase the pH values the carboxyl groups were partly neutralized by sodium, potassium or ammonium hydroxide solutions, 50 - 70% of the carboxyl groups being neutralized. The styrene - maleic anhydride copolymer (the ratio of the styrene and maleic anhydride units being I:I) was hydrolyzed by warming in water, and as a result the sterene-maleic acid copolymer was obtained. The polyelectrolite solution pH, equal 3, was increased up to 4,5 - 5,5 by neutralizing with the same bases as in the case of the polymethacrylic acid. The corroded layers are removed by putting IO-I5% viscous polyelectrolite solutions on the to be cleaned area of the object's surface. When the vertical surface is cleaned, in order to prevent the liquid from flowing down, some fibre material or a thin cloth is put on the polyelectrolite layer.

The film is removed after the water evaporates. It contains some salts of the polymethacrylic and maleic acids resulted from the reaction with the metals oxides or the carbonates. When it is necessary to remove a thick crust of layers, the treatment with the polyelectrolite solutions is repeated several times till the surface of the object becomes clean. The technical conditions affecting the process of removing the layers from the surface of different materials - the concentration, the solution viscosity and pH, the film thickness - were elaborated by experimenting on samples having layers similar to those characteristic for the museum objects.

In the laboratory of scientific conservation of stone and restoration of sculpture this method was put to the test on some model samples of sculpture materials. The examination of the influence the cleaning composition has on limestone showed that the cleaning procedure is effective.

The gradual, layer after layer process of cleaning was tested on fragments of marble and limestone sculptural and architectural articles from ancient Chersonese and on some fractures on a part of Currodini's statue "Religion".

In the Hermitage laboratory of scientific restoration of applied art works this method was tested on some original samples of antique ceramics. The samples were found in the course of archaeological excavations of a Greek town in northern Prichernomorye. There were some irregular excrescences of carbonate layers on the ceramics surface. The soil carbonate excrescences were successfully removed with the polyelectrolite

films on the bases of polymethacrilic acid partly neutralized.

This method is also effective in treating the metals with a partly or completely corroded surface. Corrosion layers on cast iron and steel, oxides and carbonates on copper and bronze surfaces which distort and destroy an applied art relic are removed practically completely after applying the film 3-IO times.

The conditions and the technique of using the film on samples having been mastered, we began to apply it to the museum objects.

A knight's fighting gauntlet (century, Germany) richly inlaid with gold was covered with a thick loose corrosion layer which was spread almost over all the gold patterns. The numerous leathern straps on the gauntlet prevented our using any known chemical or electrochemical methods. The polymer solution 2-3 mm thick was brushed on a piece of the surface 5 x 5 cm^2, preliminary slightly wetted. A polymer layer of lesser thickness after the water evaporation would be diffi- cult to remove from the metal surface. To put thicker layers is economically inexpe- dient - it takes more time for drying, requi- res more material expenditure and, as was mentioned above, only those polymer carboxyl groups take part in the reaction which are in direct contact with the surface corroded. The polymer layer was fixed with some cloth on the complex relief of the article. The fixing material must be hygroscopic, elastic and cheap. The plates of knifht's gauntlet covering finger phalanges were treated each separately, especially in the places where the plates overlap. In this way all the external surface of the gountlet inlaid with gold was treated.

Similar work was carried out in restoring a hunter's daggerhilt (beginning of the I9th century, Russia), a samovar (first quarter of the I9th century, Russia) and some other objects.

The restoration method offered is one more working tool for the restorer and in many cases is an indespensible one.

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THE RESTORATION OF BRONZE MONUMENTS IN GERMANY

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Summary

In 1968 it became obvious that bronze monuments suffer
considerable damage from aggressive components of the
air. A research project revealed the cause of corrosion,
the reactions on the surface of the metal and the forma-
tion of corrosion products. From these experiments it was
possible to propose methods for cleaning and for coating
the surface to protect the monuments from further dam-
age. Since 1968 nine important monuments from the Mid-
dle Ages and the 16/17th centuries, a large number of mon-
uments from the 19th century and modern sculptures from
the 20th century have been restored. For cleaning, mecha-
nical removal of the crust from the surface by means of
a scalpel is preferred, but cleaning pastes, which soften
the crust, are also in use. For protection of the surface,
acrylic lacquers and silicone products are preferred: waxes
have not proved to have sufficient resistance against weath-
ering.

1. Early experience of the conservation of bronze monuments.

The problem of the corrosion of bronze monuments was
already known in the 19th century. In 1864 the condition
of bronze in several large towns in Germany was examined,
to discover that polluted air causes not only an unpleasant
black appearance but also intense corrosion of the metal.
Methods of cleaning, both by washing as well as by use
of potassium hydroxide, were proposed and practised over
some decades. But these early experiences got lost in Ger-
many by the beginning of this century and, apart from
some exceptions where sculptures were regularly cleaned
with water, nothing was done for their maintenance over
more than 60 years. When, in about 1960, one became
aware of the decay of stone and medieval glass paintings
by air pollution, bronze objects were also examined in or-
der to get a general idea of their behaviour in urban at-
mospheres. The first objects analysed revealed deep corro-
sion of the metal, both by pitting to a depth of several
millimetres and by wear of larger areas of the surface,
leading for instance to complete loss of the engraved sur-
face. This instigated a research project by which, using
modern methods for study of the corrosion of metals, the
attack on bronzes of air pollutants in different environ-
ments was studied, on test specimens as well as on monu-
ments. From these experiments methods for cleaning and
surface protection were elaborated and have been applied
since 1968 on monuments and sculptures.

2. The restored monuments.

Since 1968 the following early bronze monuments have been
restored in Germany:

year of restoration	object	date	place
1968	4 puttos	1640	München
1972	Hl. Michael	1588	München
1973/74	Mars, Venus, Cupid	1585	München
1975	Cathedral Door	1066	Augsburg
1978	Fountain	1589	Nürnberg
1979	Arsenal Group	1609	Augsburg
1980	Lions, Residence	1597	München
1980	Otto v. Wittelsbach	1610	München
1981/82	Lion	1166	Braunschweig

Additionally, some important bronze sculptures from the
19th century, for example, the gilt angels on the victory
columns in München and Berlin and on the castle of Char-
lottenburg at Berlin, were restored. Finally, a large number
of sculptures of the 19th and 20th centuries in museum
gardens were either completely restored or permanently
treated to maintain their original appearance. In the fol-
lowing, the most essential of the treatments for outdoor
bronze are described.

a. The four puttos from the St. Mary column in München.

These four puttos had to be removed from position in 1968,
when the whole monument had to be restored. They were
cleaned mechanically by intense brushing and washing, re-
moving both the crust of soot and the corrosion products
until the metal became visible. The surface was then trea-
ted with beeswax. After that they were brought back to
their original place. The layer of wax disappeared after
some months and was not renewed. Since that time they
have developped the usual dark appearance but neither soot
nor the development of green corrosion products spoil the
surface.

b. Saint Michael on the facade of St. Michael's Church in München.

On this sculpture thick layers of soot had been deposited
and it was feared that serious corrosion phenomena would
exist, just as on the puttos described above. The layer of
soot was carefully removed with a scalpel, this proving not
to be a difficult matter for below the black crust a layer
of green patina was still intact and was used as an indica-
tion to stop removal. Only on a few spots was the black
surface layer in direct contact with metal. At these spots
the black layer was completely removed down to the metal
in order to prevent further corrosion by those components
of the black crust that during the preliminary tests proved
to be extremely agressive. After cleaning, the whole surface
was coated with a mat acrylic lacquer on those parts which
were much exposed to weathering. The less exposed parts
were protected by a commercial wax which had proved to
be relatively resistant to weathering. Since the sculpture is
placed in a niche of a facade, both the coating of lacquer
and of wax are still intact 11 years after the treatment
and soot can be removed by gently brushing the surface.

c. The bronze door of the cathedral of Augsburg.

This door is made of 35 cast bronze plates in relief, fixed
with nails on to a wooden frame. The plates were removed
from the frame and cleaned with warm water and a soft
brush. To protect the surface the plates were treated with
molten paraffin brushed on to the gently heated metal. As
alternative techniques, ultrasonic cleaning and application
of the paraffin in solution were discussed. Eight years after
the treatment the condition of the bronze plates on the
door, which is not struck directly by rain, is still satisfying.
The deposited soot and dust can be removed by brushing.

d. Renaissance bronzes in München, Augsburg and Nürnberg.

A series of bronze groups and fountains from the Renais-
sance period were restored by a private enterprise. From
the economic point of view the use of the scalpel is not
advantageous, especially if the objects have a detailed sur-
face. Instead, a paste was developed for cleaning. This
paste, whose effect is based on complexing agents, is ap-
plied to the surfaces. The layer of soot is softened by
the paste and can be removed with water and brush. The
green corrosion products are removed almost completely so
that normally an artificial green patina is added to improve
the appearance. Since all the objects treated in this way
remain outdoors, completely exposed to weathering, a pro-
tective coating based on silicones is applied. Filling of the
interior of the sculptures with polyurethane foam is proposed

e. The Lion of Braunschweig.

The oldest German bronze sculpture, exposed outdoors until
1980, is the Lion of Braunschweig, dated 1166. Preliminary
examinations revealed thick layers of soot on the surface,
cracks running through the body, and burst parts, obviously
destroyed by rusting iron. Because of the importance of
this sculpture it was decided to carry out a thorough resto-
ration. This lasted two years.

The Lion was removed from its socket and brought into the

workshop established for its treatment. The black deposits were removed mechanically with the scalpel, following a green layer of patina below the dark crust. Like other objects, on some parts there was no green patina between soot and metal. At that time it was decided that the Lion could not be left outside any longer because of weak stability due to improper casting techniques. To provide long-lasting stability while in a building without a stable climate, even with a temporarily unfavourable one, the surface and interior were treated with benzotriazole and finally with a 1 % solution of Paraloid in trichloroethane.

f. Restorations of monuments from the 19th century.

Monuments from the 19th century suffer no less decay than older ones. Contrary to early bronze sculptures, the monuments from the 19th century frequently show problems of stability because of rusting of the iron scaffolding in its interior. Urgent preservation became necessary to prevent the sculpture of a Victoria on a high column from falling down when it was noticed that the iron rod connecting the sculpture with its base had already lost a considerable quantity of metal by rusting. When the sculpture was brought down to the ground it was found that the iron bars inserted originally for stabilisation had corroded deeply. Furthermore, some parts of the sculpture, such as the one leg on which it was standing, showed large cracks due to the increase in volume of the rusting iron. It was therefore necessary to replace the whole original iron scaffolding by a new one made of stainless steel and to remove also those parts of the bronze which had lost their stability.

A great number of sculptures from the 19th century, especially those like a Victoria, are gilt. Analysis of this surface showed that there was no serious corrosion which could be attributed to electrochemical dissolution of bronze in contact with gold. The gold was perforated in places and at these points the bronze below was pitted. This relatively weak electrochemical reaction on the surface of gilt bronzes leads to the belief that bronzes could still be gilded in future: it could be considered as a protective coating for the bronze. This gilding was done using gold leaf, with drying oil as an adhesive medium.

g. The care of museum sculptures from the 19/20th century.

Most of the modern art museums have some bronze sculptures in the open. These suffer from the same corrosion and pollution phenomena as objects from earlier periods. The main problem is loss of the artificial patination, of the original appearance of the surface as determined by the artist. Therefore, various efforts have been made to maintain the appearance of the surface. Regular washing and application of waxes has not proved efficient in practice. For this reason, acrylic lacquers have come into use more and more since ten years ago. Until now they have remained intact on clean metal surfaces as well as on artificially patinated bronzes. The change in appearance of the object is almost imperceptible. On the earliest applications of acrylic lacquers it is now evident that the loss of protection starts on the more bent parts, where the layer of lacquer was probably thin. This necessitates a repetition of treatment of these parts.

3. Conclusion.

From the restoration of a series of bronze monuments from the Middle Ages and the 16/17th centuries, together with the treatment of a great number of sculptures from the 19/20th centuries, it is obvious that mechanical cleaning, removal of the layer of dirt and soot by scalpel, though most efficient, is time consuming. In order to save time the application of cleaning pastes is possible. For protection of the surface, waxes are only effective on those parts which are not much exposed to weathering. For those objects which are completely exposed, acrylic lacquers have proved to be resistant over more than 10 years. Regular cleaning of bronze sculptures by washing prevents corrosion but alters the appearance of the surface by darkening and the formation of green spots and stripes. Oil-gilding, which was common for some types of sculpture in the 19th century, is considered to be protective.

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INTERPRETATION THROUGH RECONSTRUCTION OF A RUSTED 10TH CENTURY VIKING IRON SLIDING KEY

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SUMMARY

A non-destructive method for the interpret
ation of the construction and surface tex-
ture of archaeological metal-work is descri-
bed. Prior training as a jeweller and silver
smith followed by many years of conservation
of artifacts suggested a need to be able to
compare artifacts of ancient type but in
modern, as used, condition. Museums in
several European and East European countries
were visited and Ustredi Umeleckych Remesel,
Prague, provided the opportunity to develope
the theory into practice. The result prov-
ides a method which may be adapted to record
obscure information that may be present in
many artifacts, and to indicate the type of
tools necessary to create the appearance and
nature of the piece. Silicone rubber moulds
were taken from the original Viking Key and
an electrotype copy formed. The copy contain
ed detail which indicated the method of its
manufacture 1000 years ago, so that the Iron
smith at U.U.R. was able to make a modern
Viking Key, and provide documentation to
relate to excavated iron-working tools and
artifacts.

Scientific apparatus can provide information
about the various matallurgical and chemical
structures that are contained within ancient
metalwork. Archaeology has indicated the
manner in which metals were worked at
various periods of history. What remains for
us to study visually, however, is usually a
piece of corroded, incomplete, damaged metal
to which we give the name "artifact" and a
description if we can decide what it was. No
scientific apparatus will enable us to see
the whole object as it was, nor let us
handle and use it as it was when made.

Technological interpretation of antiquities
is now fashionable. Many methods of study
are being practised. Reconstruction of
damaged artifacts by heating, soldering and
bending may be used to re-create the form of
the original antiquity. This manipulation,
however, changes the structure of the metal.
Information pointing to the history of the
object is lost and it becomes virtually use-
less for further analytical research.

For many years I have made electrotype (gal-
vanoplastic) reproductions of artifacts for
technological study in place of the antiquity
itslef. The reproductions can be manipulated
as desired without causing any destruction of
the historical content of the original.

This paper explains an extension of this
truly non-destructive method of interpreta-
tion. From the detail contained in the
electrotype of a complicated iron key the
manufacturing process could be reconstructed

and a copy in iron made. By this means all
of the hidden implications of the corroded
object could be brought to light to serve as
a basis for subsequent consideration.

For the re-creation of the working artifact
we must depend upon the skill of the crafts-
men whose ability and practised use of eye,
hand and mind fills the gaps for which elec-
trical apparatus cannot provide answers. The
result of the craftsman's work can then be
assessed in scientific terms or be discussed
by the common man because it is there for
examination. Comparisons can also be made
between several aspects of technology.

Copying of the Viking Key establishes a non-
destructive method for comparative techno-
logy based upon the traditional methods
that continue in certain workshops to the
present day.

The important ingredient of this project was
the attitude of the Ustredi Umeleckych
Remesel (Craft Centre) Prague. U.U.R. is
not widely known. In 1974 I was recommended
to visit it by a Danish Conservator, Eli
Andersen, of Skive. My visit in 1976, as an
Exchange Specialist, was supported by the
British Council. U.U.R. was established in
1952 by the Czech Government with the pur-
pose of perpetuating ancient skills and
traditional crafts and techniques. Its
craftsmen are all highly skilled and know-
ledgeable in the historic background of the
materials in which they work. Of 53 work-
shops throughout Czechoslovakia I chose to
visit the Ironsmiths in Prague. I was most
impressed by the attitude towards working
the metal and their ability to make intri-
cate designs and mechanisms: a rose-bud from
a single piece of iron; wrought-iron gates,
for example.

I had no doubt that, from experience, the
smiths would be able to select the methods
and tools by which a particular piece of
iron-work could be made. It was upon this
competence that success of the research
would depend. I am sure that many black-
smiths could make a copy. Few, however,
would have the advantage of doing so as a
continuation of their daily tasks, using
primitive and traditional hand-tools only,
without electric drills, oxy-acetylene weld-
ing, etc., in a workshop devoted to produ-
cing replacements of iron-work for histor-
ical monuments such as castles of the fif-
teenth century: the replacements to be com-
parable with the originals.

We discussed methods of technological inter-
pretation. The then Director accepted a
small research project. It centred around
making a copy of a piece of ancient ironwork
in traditional manner and keeping a record
of the tools and methods used, and of the
time taken for each task.

For this research project I made an electro-
type reproduction of a Viking Iron Sliding
Key, recently excavated, 1977, from Copper-
gate Viking Site, York. I was permitted to
make moulds of silicone rubber so that as
much detail as possible should be included.
The original was, ofcourse, corroded so that
even slight surface marking was important.
The original weight of the metal had to be
estimated to provide the correct dimensions
for authenticity.

The electrotype reproduction was sent to
U.U.R. where their Master Smith, Rudolf
Polak, studied it and worked out a manufact-
uring process by which the original could
have been made.

My project accepted, it was fitted into the
U.U.R. programme of work. Eventually, on
11th February, 1981, I visited U.U.R. Head-
quarters in Prague and was presented with
the documentation of the tools and proces-
ses used, including illustrations, together
with the "Masterpiece" copy of the Viking
Key as proof that it could be made.

The documentation lists the sequence of
operations, with times in seconds, for hot-
and cold-working on the iron; with names of
tools, uses and purposes. Less preferable
alternative methods are mentioned. Oper-
ations are illustrated so that one can
imagine the action even if lacking experi-
ence as a blacksmith. The ease with which
iron may be worked when hot, as opposed to
when cold, is made apparent by remarks as
"No.4. punching the round hole in eye".
Most of the work was done with the iron in
'plastic-state' at high temperature. The
grain of the metal is deformed into shape
and not severed as happens with modern
drills, saws and files. The illustrations
indicate the simplicity of the traditional
processes - difficult for the uninitiated
to recognise in a finished object.

By following the sequence of operations one
can understand the gross changes made to
the metal. The characteristic results may
then be recognised on other pieces of metal-
work, and tools for them may be inferred.
The smaller changes that create surface
patterns need to be considered seperately:
references appear in the Bibliography.

The time taken to make the Key copy, namely
two hours fiftyseven minutes, is valuable
information against which to compare other
activities. By discovering the size and
weights of the tools needed to make this
particular Key, weighing 32 grammes, it
becomes possible to form realistic opinions
about the type of work that might be expect
ed from the blacksmiths' tools excavated at
York and from elsewhere. Other concepts,
about uses, trade, markets, supply of mat-
erials, can then be developed. The method is
of general application.

A research programme of a series of pieces,
each progressively larger, is envisaged.
This would allow comparisons between the
size and weight of tool, time and heat
needed to create a variety of artifacts,
and so assess the capacity of a collection
of tools and equipment as excavated. It
would also indicate the amount of 'back-up'
services required for a given weight and
complexity of artifact. So we have a two-
fold research project. One to indicate
how an artifact could have been created;
the other to indicate with what it could
have been achieved.

Completion of the project in February 1981
enabled a copy of the Viking Iron Sliding
Key to be presented to Her Majesty Queen
Margarethe of Denmark at the opening
ceremony of the Viking Exhibition at Brede,
Denmark, in April 1981.

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The photograph of the three Keys A. B. C. show the similarity of appearence even allowing for the fact that the electrotype reproduction was made from moulds taken before the original was cleaned for exhibition. This indicates the perceptive qualities of the Ustredi Umeleckych Remesel Blacksmith.

Plate one.
A. Original Iron Key. Small find no.1977. 7.1911. In conservation-cleaned condition.
B. Electrotype reproduction; corroded condition 'as excavated'. Sent to U.U.R. 1978.
C. Ustredi Umeleckych Remesel modern Iron Key copy following the detail in the electrotype reproduction. Received with documentation 11 February, 1981.

The accompanying plates illustrate the manufacturing processes numbered to relate to the 'Specification of sequence of documentation' on the last three plates. The selected processes may be applied to other iron-work so that a method of manufacture might be imagined or indicated. The fact that a Key has been produced allows for processes to be compared with each other against the original which remains undamged for total reference.

A   B   C

mm 1|0   2|0   3|0   4|0   5|

VIKING KEY COPY

Tools used.

Some operations, numbered, in the 'Specifications of sequence of operations'.
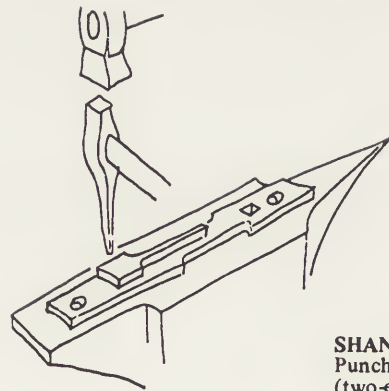
SHANK 4
Punching of round hole in eye (two-ended drift hammer)
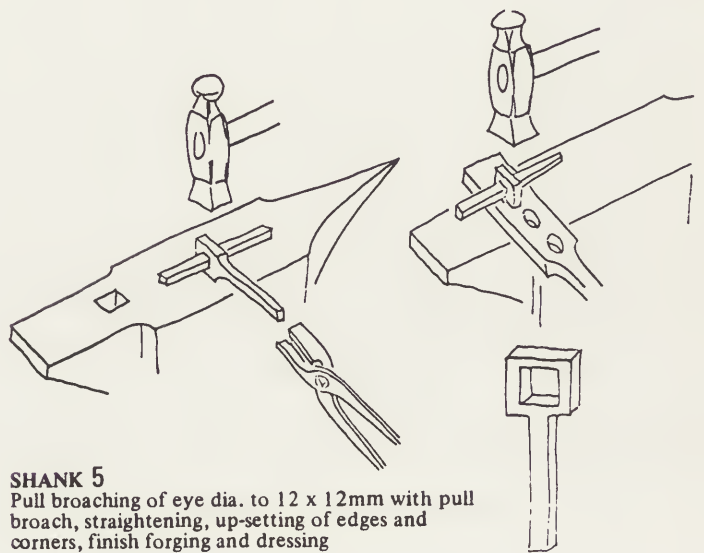
SHANK 5
Pull broaching of eye dia. to 12 x 12mm with pull broach, straightening, up-setting of edges and corners, finish forging and dressing
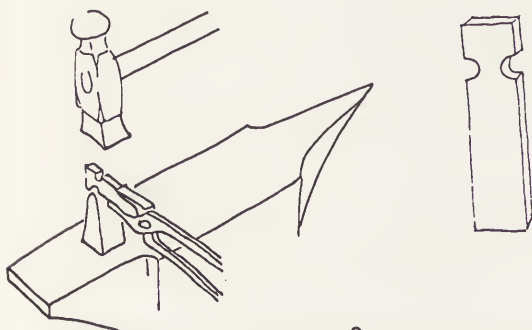
SHANK 2
Separation of eye and shank – rough forging 5 x 5mm – flattening of eye.
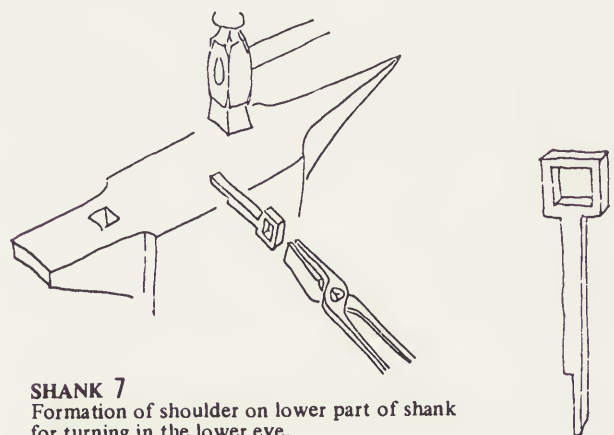
SHANK 7
Formation of shoulder on lower part of shank for turning in the lower eye.
Dressing of whole shank.
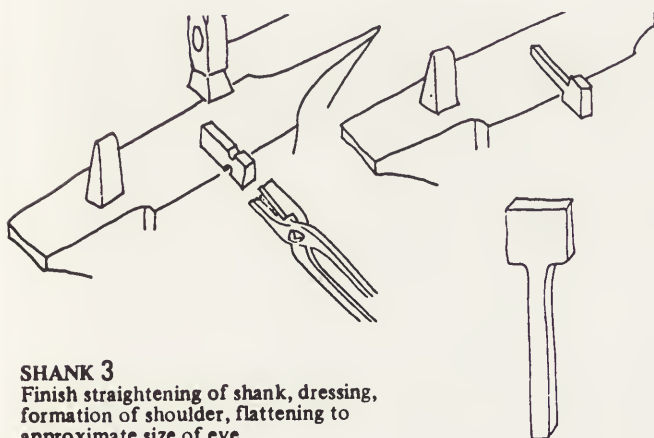
SHANK 3
Finish straightening of shank, dressing, formation of shoulder, flattening to approximate size of eye.
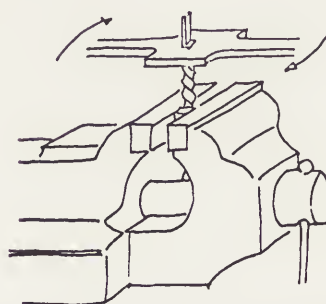
SHANK 9
Torsional working of shank by 3 turns.
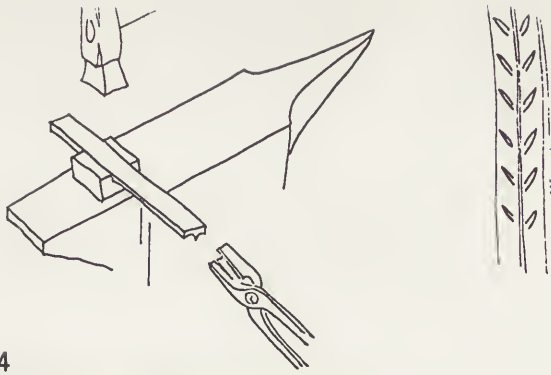
CAGE 14
Forging-off of ornamental element in anvil swage.
Straightening of parts, identical lengths, parting-off
of lengths from forged blank.
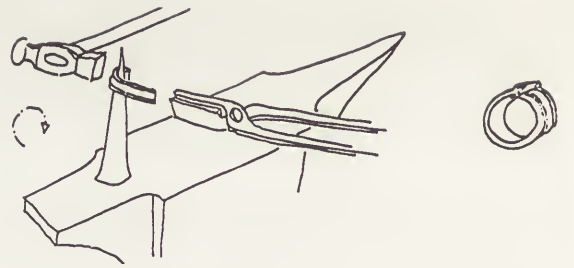
COLLAR 26
Scrolling of rings, thinning-down of bent-over ends.
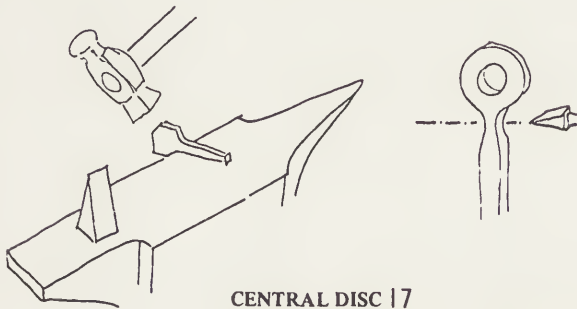
CENTRAL DISC 17
Shoulder 3mm thickness – round blank
Punching dia. 5mm rounding-off of shape
Pull broaching to dia. 8mm.
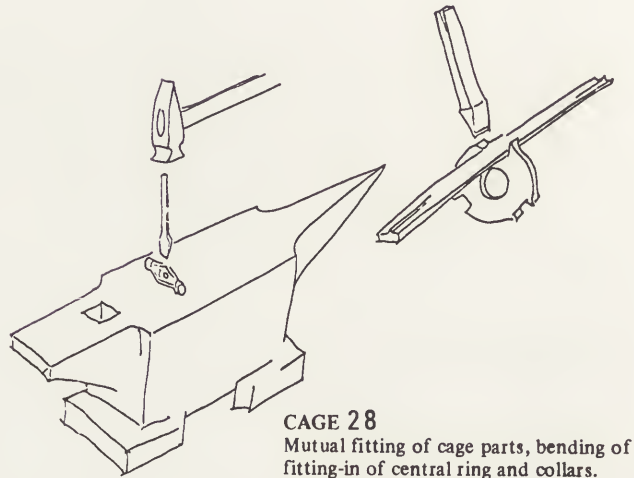
CAGE 28
Mutual fitting of cage parts, bending of rods,
fitting-in of central ring and collars.
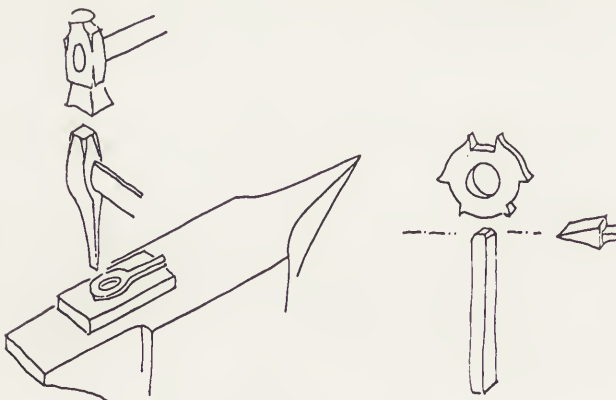
CENTRAL DISC 22
Chiseling of 3 slots, dressing, parting-off from stock.
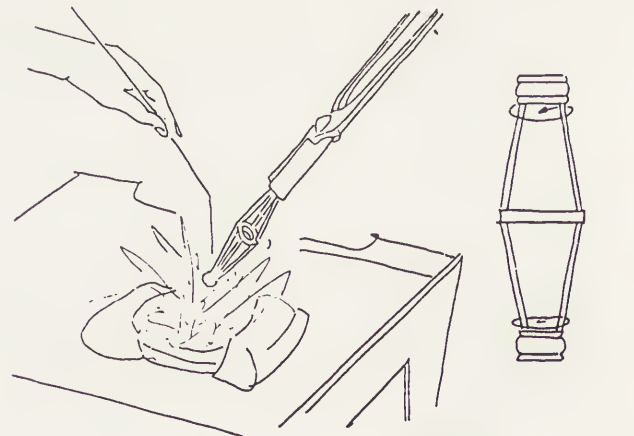
CAGE 30
Soldering of cage collars.
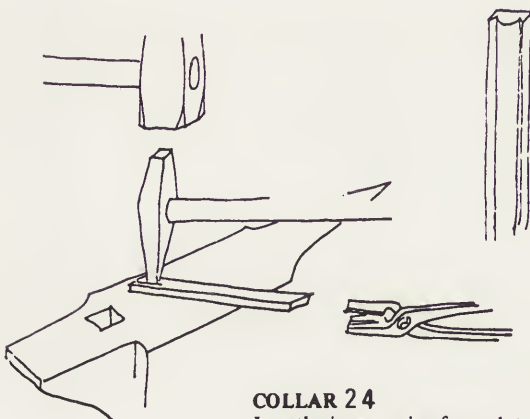
COLLAR 24
Lengthwise grooving from slots
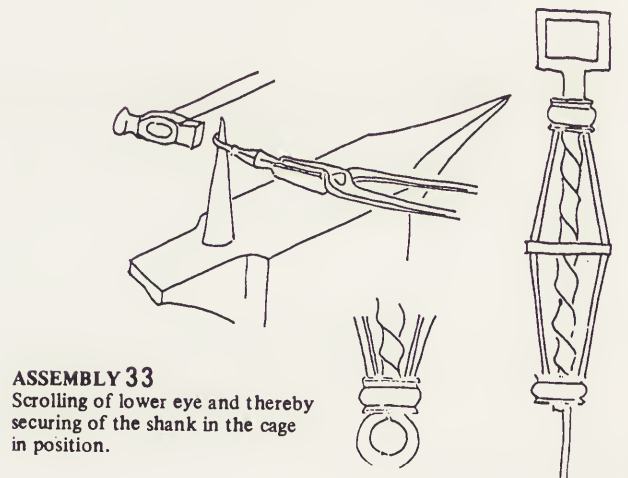
ASSEMBLY 33
Scrolling of lower eye and thereby
securing of the shank in the cage
in position.

Viking Key - Specification of Sequence of Operations

Ko.	Part	Material	Tools -Equipment-Place	Method	In time sec. Heating		Operation	Note
1	shank	FE-class 10 10x10x50	hearth, anvil, anvil cutter, hammer 2 kg, tongs	M	65	25	separation from bar - profile selected intentionally - work envisaged to be performed from original square Fig.1	preparation for manufacture
2	"	"	anvil, hammer, round anvil stake, mm straight tongs	H	30	30	separation of eye and shank - rough forging 5x5- flattening of eye Fig.2/1, 2/2	on anvil stake, on anvil flat surface (anvil face)
3	"	"	"	H	30	30	finish straightening of shank, dressing, formation of shoulder, flattening to approximate size of eye Fig.2/2	on flat surface of anvil (anvil face)
4	"	"	anvil, heading tool, drift hammer dia.5/10, hammer, straight tongs	H	40	45	punching of round hole in eye (two-ended drift hammer) Fig.4	upon hole in heading tool, on flat surface of anvil (anvil face)
5	"	"	anvil, heading tool, mandrel 8x8/12x12, hammer, tongs	H	65	60	pull broaching of eye dia.to 12x12 with pull broach, straightening, upsetting of edges and corners Fig.5	in heading tool and on flat surface of anvil
6	"	"	"	H			finish forging and dressing	on flat surface of anvil (anvil face)
7	"	"	anvil, hammer, tongs	H	40	35	formation of shoulder on lower part of shank for turning in the lower eye Fig.7	on flat surface and edge of anvil
8	"	"	"	H	40	60	dressing of whole shank	on flat surface of anvil
9	"	"	vice, wrench (straight tongs) 120mm	C		100	torsional working of shank by 3 turns Fig.9	eye clamped in vice - shank in wrench (operation in hot state possible, but the spiral will not be a regular one)
10	"	"	wooden block, wooden mallet 0,1	H	30	130	compensation of potential deformations	originally may not have been reckoned with
11	key case	FE-class 10 10x10x50	hearth, anvil, hammer, straight tongs	H	120	120	forging-off on mat.(6x x200) during first heating to 8x5 approx.160 Fig.11	on the tip and surface 07/anvil
12	"	"	"	M	120	120	"	"
13	"	"	"	H	80	60	dressing	"

No	Part	Material	Tools-Equipment-Place	Method	In time sec.	Heating	Operation	Note
14	key cage alt.1	FE-class 10 10x10x50	hearth, anvil, hammer, anvil swage, straight tongs	H	120	80	forging-off of ornamental element in anvil swage Fig.14, alt.1	hammer knocks on underside of material and its driving into anvil swage
	" alt.2	"	hearth, anvil, hammer, tongs, driver, assistant	H	150	80	forging-off of ornamental element with driving tool	hammer knocks on driving tool, material held on face by assistant, or assistant handles sledge hammer, alt.1 preferable
15	"	"	hearth, anvil, hammer, tongs, anvil cutter	H	15	30	straightening of parts, identical lengths, parting-off of lengths from forged blank Fig.17	on anvil face, measurement by comparison to shank
16	"	"	hearth, anvil, hammer, tongs	H	15	30	straightening of parts identical lengths	on anvil face
17	central disc	FE-class 10 10x10x50	anvil, hammer, straight tongs, hearth	H	45	60	shoulder 3 mm thickness - round blank	on anvil edge
18	"	"	anvil, hammer, straight tongs, hearth, heading tool, drift hammer	H	60	60	punching dia.5 rounding-off of shape	in heading tool above aperture in anvil
19	"	"	anvil, hammer, straight tongs, hearth, heading tool, mandrel	H	60	30	pull broaching to dia.8	in heading tool
20	"	"	anvil, hammer, straight tongs, hearth, anvil cutter	H	20	30	parting-off from stock	
21	"	F	anvil, hammer, straight tongs, hearth	H	30	20	dressing	on anvil face and with mandrel
22	"alt.1 "alt.2	: :	vice 120mm, file 20/5 anvil, chisel 5mm, bolster	C H	540 240	- 25	filing of 3 slots for cage bars chiseling of 3 slots Fig.22	on cushion, edges left bent-over for assembly - alt.2 preferable
23	collar	FE-class 10 10x10x50	anvil, hammer, hearth, straight tongs	H	120	120	mt.offset for subsequent work to 8x5	on anvil face
24	alt.1	"	anvil, hammer, hearth, straight tongs, chisel assistant	H	150	60	lengthwise grooving from slots Fig.24	on anvil face
	alt.2	"	anvil, hammer, hearth, straight tongs, anvil swage	H	150	60	grooving in anvil swage-see item 14	more up-to-date - alt.1 preferable
25	"	"	anvil, hammer, hearth, straight tongs, hardy	H	30	30	parting-off of parts	

No	Part	Material	Tools-Equipment-Place	Method	In time sec.	Heating	Operation	Note
26	collar	FK-class 10 10x10x50 2x	anvil, hammer, hearth, straight tongs, filing block	H	30	30	scrolling of rings, thinning-down of bent-over ends Fig.26	on filing block and anvil face
27	"	" 2x	anvil, hammer, hearth, straight tongs, mandrel dia.8 mm	C	300		dressing of collars - straightening	
28	assembly of parts	cage assembly	vice, hammer, mandrel, file	C	3600		mutual fitting of cage parts, bending of rods, fitting-in of central ring and collars Fig.28	
29	"	"	vice, hammer, flat hand chisel 10 mm	C	600		cutting of central ring edges	
30	"	"	hearth, tongs, Cu wire 1 mm - borax (formerly glass or quarz sand)	H	300		soldering of cage collars Fig.30	
31	"	"	wire brush - file dia.6 and 5x5	C	300		removal of Cu residues	
32	"	assembly of key	vice	C	180		threading of shank with eye through the cage, trial run	
33	"	"	hearth, filing block, hammer	H moderate	180	20	scrolling of lower eye and thereby securing of the shank in the cage in position Fig.33	
34	"	"	surface finish in oil	H moderate	600	20	soaking, polishing, application of rust inhibiter	

Special Tools

1 anvil swage steel 30/30/50			hearth, anvil, hammer, chisels, tongs	H	2400	1600	forging-off of basic shapes, engraving of ornaments, can be un-hardened	
2 " "			"	H	2400	1600	knocking-off of pattern, hardening, dressing	

3 the remaining tools are not special ones and their dimensions are indicated in the drawing

H = hot operation   C = cold operation   Fig. = obr.

Worked out by: Rudolf Polák, master of art handicraft (signed)

Prague, Oct.20, 1980.

ÚSTŘEDÍ UMĚLECKÝCH ŘEMESEL
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THE APPLICATION OF NEW MATERIALS TO THE CONSERVATION OF FERROUS METALS IN A MUSEUM COLLECTION

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SUMMARY

Herein there are xonsidered methods of conservation of ferrous metals. There are given the results of testing physico-chemical, protective and electrical chemical properties of conservation materials: waxes (beeswax, cerisine), polymer films (polybutyl metacrylate and polyvinyl butyral) and inhibited film-forming materials (the Mobil autoconservant, NG-222B, NG-216C). It was shown that inhibited film-forming compositions exceed, in a complex of properties, traditional materials used in the restoration of metals.

One of the principal problems in the museum practice is the necessity to prevent corrosion of exhibits of ferrous metals.

Museum exhibits are kept in an atmosphere whose humidity ranges from 40% to 80% in the unheated period (July-September). The surface of most museum exhibits of metal can be classified as "slightly corroded", the critical humidity for which constitutes 65%, i.e. under such humidity a corrosion process begins on an unprotected surface of exhibits.

Objects are coated with protective compositions having an organic base at the final stage of the restoration treatment in order to prevent corrosion. Oils, lubricants, microwaxes, beeswax and film-forming coatings are applied for conservation in the restoration practice. The choice of a conservation material is determined not only by aesthetic considerations, but also by the conditions under which the object will be kept.

The principal protective material for a long-term storage of wxhibits have, until recently, been plastic lubricants which protect metal from corrosion only if they are applied in the form of a 2-5 mm. coat. They are labour-consuming during the process of conservation and taking out of conservation, and spoil the outward appearance of objects.

Film-forming compositions, based on polymers of the polymerization and condensation type, have lately found wide application. Particularly popular are colourless lacquers - polyacrylates, polyvinyl butyral, copolymers of polyvinyl acetate with polyvinyl chloride, alkyd and other types of lacquers. The majority of restorers give preferrence to acryl lacquers. The protective properties of the above-listed materials are, however, insufficient, because any slight destruction of the film allows moisture and agressive substances (O_2, SO_2) to penetrate under the film, and a corrosion process begins.

It should be observed that conservation materials do not, as a rule, contain corrosion inhibitors, or contain low-effective screening inhibitors. Such inhibitors include high-molecular fat acids, ether of these acids with alcohols, soaps of fat acids and oxidized microwaxes. Screening type inhibitors are physically adsorbed on the metal surface, forming an oriented layer of molecules, owing to which the protective capability of conservation materials is enhanced. The shortcoming of screening inhibitors is the absence of an "aftereffect", as they are easily removed with solvents.

Conservation materials, employed by restorers in the museum practice, ensure the protection against corrosion of objects of art for a term of not longer than 2-3 years.

At the same time washable inhibited film-forming compositions, which are applied to the surface of objects from solvents by means of immersion, pulverization or with a brush, and removed with a solvent, are at present widely employed in the conservation of automobiles, agricultural and other machinery. Compositions of this type form, after the solvent has evaporated, on the metal surface a 20-100 mkm thich semisolid film, ensuring protection against corrosion for a term of 10-15 years when objects are kept inside, and up to 5 years when kept outside, in the open air.

Compositions of washable inhibited coatings include polymer resins, microwaxes, bitumens, water- and oil-soluble corrosion inhibitors and solvents. Among them there are, apart from screening inhibitors, chemisorption inhibitors. Such inhibitors include organic chromates and nitrites, alkyl benzolsulphanates of calcium, magnesium and barium, alkenyl succinimide and others. In so doing the screening inhibitors ensure a rapid dehydration of the metal surface. A sorption of the chemisorption type inhibitors takes place on the surface freed from water. When donor and acceptor inhibitors are used simultaneously, strong chemisorption films are formed both on negatively and positively charged parts of metal. Chemisorption films are then added a layer of screening inhibitors, thus forming the so-called "sandwich" structure. The presence of corrosion in the composition of inhibitors ensures a formation of a strong absoption-chemosorption coat on the metal surface.

An indisputable advantage of coatings of this type is their capability to protect metal from corrosion in a thin layer for longer periods, as well as the simplicity of their application and removal. It is owing to this that inhibited film-forming compositions succeed in replacing plastic lubricants, waxes and other uninhibited material in various fields of technology.

Inhibited film-forming compositions are widely employed throughout the world in the conservation of metal objects. They are manufactured by petroleum companies of the majority of developed countries.

The Mobil autoconservant, NG-222 B-type and NG-216 C-type compositions have been selected with the aim of finding a possibility of using inhibited film-forming compositions in the conservation of museum exhibits. These coatings are designed for conserving hidden and difficult of access metal surfaces, in particular, hidden surfaces of automobiles, as well as for a long-term conservation of spare parts.

The investigation of the properties of the above-listed materials has been conducted by comparing them with traditional materials, used in restoration previously. The following were selected - 10% ceresine dispersion in white spirit, 5% bleached beeswax dispersion in turpentine, 8% polyvinyl butyral solution in ethyl alcohol and 10% polybutyl metacrylate solution in ethyl alcohol and 10% polybutyl metacrylate solution in xylol. The concentrations of these solutions and dispersions were chosen on the basis of the practical experience in metal restoration.

A complex of well-known techniques for testing physico-chemical, protective and electrochemical properties was employed for a comparative evaluation of the properties of new and traditional materials.

Table 1 gives the results of testing physicochemical properties of inhibited and uninhibited materials.

As can be seen from the Table, all the materials under investigation, except for ceresine dispersion and polyvinyl butiral solution, wet the metal surface well, which is proved by the results of the determination of spreading and the height of rising up the microgap.

Beeswax dispersion has a high water-displacing capability, impregnates iron oxide powder well, but does not protect at all the metal surface, wetted with a natrium chloride solution. The dispersion protects a clean metal surface at high humidity and temperature for three days (Table 2).

Polyvinyl butyral solution displays a better water-displacement as compared to polymer materials, but has an insufficient wetting and impregnating capability. The results of the determination of natrium chloride displacement show that polymer materials are slow-acting.

Films of inhibited waxes and polymer materials have a low level of protective properties both at high humidity and temperature, and in the aggressive medium of sulphurous gas for the reason that they insulate the metal surface mechanically only.

The Mobil autoconservant, NG-222B and NG-216C compositions are low-viscosity products which spread easily over a metal surface, penetrating into microgaps and cracks. The compositions displace water and agressive electrolyte from the metal surface, which is shown by the properties "displacement of 3% NaCl solution". The Mobil autoconservant and NG-216C composition have a higher level of surface properties and an ability to penetrate corrosion products than NG-222B composition. After the evaporation of the solvent the compositions form on the metal surface a thin film, elastic at -40°C, and which does not flow off a vertical surface at +70°C. The film of the coatings is of yellow to pale brown colour and has a slight adhesiveness.

The test results of protective properties show that the film of the Mobil autoconservant and the NG-222B composition protects metals against corrosion in the G-4 thermal moisture chamber for more than 48 days, in

Physico-chemical properties of conservation materials

Table 1

Ser. Nos.	Properties	Beeswax	Ceresine	Polyvinyl butyral	Polybutyl metacrylate	Mobil autoconservant	NG-222B	NG-216C
1.	Viscosity by VS-4, c	12.1	-	307	11,5	18	20	12
2.	Active substance content, in % mass	5	10	8	10	40	40	26.5
3.	Rise height up the microgap (steel 10, 2 hrs), mm	130	110	17	110	86	35	65
4.	Spreading by steel 10, 0.5 hrs, mm	33	20	13,5	29	32	22	35
5.	Water-displacement capability, d_1, mm	100	52	50	18	82	75	72
	d_2, mm	100	52	82	20,5	82	75	72
	d_3, mm	70	52	82	20,5	82	75	72
6.	Impregnation capability (Fe_2O_3), mm	13	1	1	30	8	3	8
7.	Displacement of 3% natrium solution, steel 10:							
	-product spot diameter, mm	18	10	12	35	28	21	35
	-displaced electrolyte diameter, mm	16	10	32	35	28	21	32
	-corrosion extent under the product spot, in %	0.2	0.2	0.2	0.2	0.2	0.2	0.2

Ceresine dispersion has a low level of surface properties, displaces poorly water and agressive electrolyte from the metal surface and impregnates corrosion products very little. But, owing to its finely crystalline structure, the ceresine film insulates metal mechanically for seven days.

the salt mist chamber NG-222B and NG-216C - for over 12 days, and the Mobil autoconservant - for 8 days, in the sulphurus gas chamber - 48 hours (Table 2).

The toxicity of the NG-216C composition should be regarded as its drawback, since trichloroethylene is used as a solvent.

Table 2

Protective properties of films of conservati   on materials

Ser. Nos.	Properties	Beeswax	Ceresine	Polyvinyl butyral	Polybutyl metacrylate	Mobil autoconservant	NG-222B	NG-216C
1.	Protective properties in the G-4 thermal moisture chamber, steel 10:							
	-time before corrosion appears, in days	3	7	6	5	42	45	25
	-extent of corrosion of the surface after 24 days, in %	100	80	30	10	0	0	0
2.	Protective properties in the sulphurous gas chamber, steel 10, after 48 hours, the extent of corrosion of the surface, in %	100	0	100	100	0	0	0
3.	Film thickness, mkm	21	35	80	10	32	35	10
4.	Anode potential (mV) in a water extract with $L = 2A/m^2$ (galvanostatic technique)	–	-350	-520	-530	+1800	+480	–

The long-term protection capability of coatings depend, to a large extent, upon the corrosion activity of electrolyte penetrating after some time to the metal surface through microdefects of the film. A shifting of the potential towards the positive field was established during the investigations of the kinetics of the anode reaction of steel dissolution in a water extract from the Mobil autoconservant, NG-222B and NG-216C compositions (Fig. 1). This means that the compositions have a capability to inhibit water in the event of its penetrating through defects of the film to the metal and slow down the development of the corrosion process at the expense of the anode polarization.

Thus, the tests results show that the inhibited film-forming compositions surpass waxes and polymer materials in a complex of properties - a capability of wetting the metal surface, displacing agressive electrolyte, impregnating corrosion products and protecting ferrous metals against atmospheric corrosion.

The preliminary testing of the Mobil autoconservant for the protection of museum exhibits from corrosion demonstrated a possibility of its practical application in museums.

It follows from the data obtained that uninhibited materials can be used for the conservation of objects detailed for an exposition, but they are low-effective for their long-term storage. It is advisable to use inhibited film-forming materials, the Mobil autoconservant and NG-222B composition whose guaranteed period of protection is much longer (3-4 times) for a long-term storage of museum exhibits.
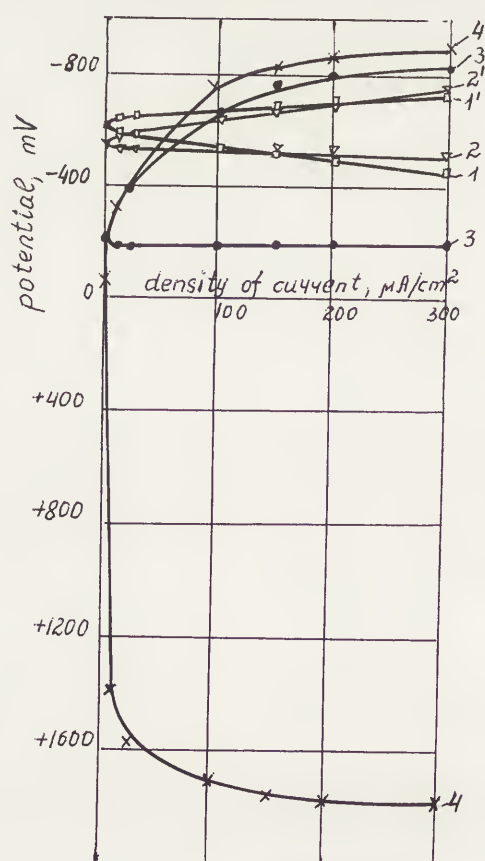
Fig. 1. Curves of Steel Polarization in Water Extracts:

2,2'. polybutyl metacrylate;

1,1'. polyvinyl butyral;

3,3'. distillated water;

4,4'. Mobil autoconservant.

Section 23

Icons

Icônes

Section 23

Icons

Icônes

RUSSIAN METAL ICONS IN THE SMITHSONIAN INSTITUTION

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SUMMARY

The author discusses the technical study, conservation and ethnographic use of the Smithsonian Institution's collection of Russian enamelled copper-alloy icons acquired in 1892.

INTRODUCTION

The basis of the Smithsonian Institution's Russian ecclesiastical collection was formed in 1892 with the accession of approximately 290 objects purchased by George F. Kunz at the annual fair in Nizhni Novgorod (now Gorky), Russia, in August, 1891. George Kunz corresponded with the Assistant Secretary in Charge of the United States National Museum, G. Brown Goode, often using Tiffany and Company in New York as a mailing address. Mr. Goode described the ecclesiastical collection as a very valuable one and regretted the lack of funds to purchase all that Kunz offered. Some of these icons and crosses are described by Immanuel Moses Casanowicz in Collections of Objects of Religious Ceremonial in the United States National Museum, 1929.

The classification, technical study, conservation and storage of the objects began in 1982 as a project jointly sponsored by the Division of Community Life and the Division of Conservation, National Museum of American History, Smithsonian Institution, which provided funding and laboratory facilities to the author. Of the 328 objects in the collection today, 228 metal icons, 54 metal crucifixes and 8 painted panel icons were accessioned in 1892.

Technical Study

The majority of the collection consists of copper alloy icons and crucifixes. The icon group has 1 tetraptych, 99 triptychs and 128 plaques from the seventeenth to the nineteenth centuries. Forty-six of these have champleve enamel in various stages of deterioration and loss. All of the objects were examined under a Wild-Heerbrug stereobinocular microscope x 10-x50.

Some icons without any enamel remains have the appearance of gilding in the crevices and a textured surface where enamel could have been received. This may indicate that they were once gilded and enamelled as were many Russian metal icons, but analytical studies are not yet complete.

One of the most interesting observations under the microscope is the quantity, shape and distribution of compacted grains of quartz and feldspar (as identified by Dr. Pete Dunn of the Department of Mineral Sciences, National Museum of Natural History, Smithsonian Institution S.I.).

Macroscopically, the icons appeared very dirty, but after examining the collection under the microscope, the following observations were made:

1) The siliceous material is not "dirt" of the type, consistency and distribution usually seen on objects under the microscope.

2) There is no admixture of other debris except for some red fibers and white fibers, tiny charred pieces of wood, and an orange-red powder.

   A sample of the red fibers from icons #25,819.196 and #25,819.282 was analyzed by Dr. Dunn. An X-ray diffraction powder pattern (using Gandolfi 114-116 mm. cameras) showed that the mineral saturating the fibers is goethite, an iron oxide used on rouge cloths. Enamel is often rubbed down with rouge cloths after firing is complete and when cleaning.

   The charred pieces of wood perhaps remain from charcoal used to fire the enamels.

   An attempt by Dr. Dunn to identify the orange-red powder using X-ray diffraction did not yield results and further studies are anticipated.

3) The siliceous material appears repeatedly, filling crevices, folds and haloes in the same pattern as did the enamel.

4) On icons where enamel is deteriorating, the siliceous material is seen beneath remains of enamel as visualized in the photomicrographic slide of icon #25,819.150.

5) Dr. Robert Brill of the Corning Museum of Glass examined 12 representative icons on September 12, 1982, and stated that the edges of the quartz and feldspar are fire-rounded. This suggests that the siliceous material may have been used as a base under the frit.

   The enamel of the icons is opaque, mostly blue and white and pock-marked with depressions. In the preface to the South Kensington Museum Catalogue (1875:b), London, it states that:
   "There is more than one kind of enamel....and they may be classed according to the methods of working and the completeness of firing. In the early enamels the vitreous paste is thick and solid, being but partially turned into glass. In these enamels the colours are pure and rich, particularly....the blues and greens, but the material is opaque and has to be rubbed down to a smooth surface after the process of firing is complete. This is the method used in the greater part of the enamelled vessels of the Chinese, the Byzantine reliquaries, crosses and sacred vessels made on the Rhine, mostly at or near Cologne, and the early manufactures of the enamellers of Limoges".

Further research into the Russian enamelling technique is being conducted. Any information or suggestions will be welcomed.

Treatment

In 1983, the author began the treatment of some metal icons whose unstable enamel and extent of corrosion made action urgent.

Green cupric chlorides were often visible and confirmed by testing with acidified silver nitrate. Cupric chlorides were excavated mechanically under the microscope and the cavities treated with silver oxide suspended

in methanol according to the method of Organ (1963).

Some icons had a grey, wax-like cuprous chloride surface deposit which was mechanically decreased with cotton swabs and naphtha solvent. The surface was then treated with silver oxide suspended in methanol. In both instances, the resultant brown color of the treated areas blended well with the patina of the metal.

A blue and white enamelled triptych #25,819.057 showed innocuous but odd-appearing, flat brown plaques in the crevices which blended in color with the patina of the copper alloy. Under x40-x50 magnification, the plaques had a separating circumference which, when lifted, revealed a deteriorated, porous pink metallic deposit in deep recesses. When the porous copper was excavated, the bottom of the pits were found to be filled with green cupric chlorides. The deterioration process resembled Leidheiser's description of dezincification (Leidheiser; 1971:79-82).

In addition to being worn on the person, metal icons were also affixed to wooden crosses in cemeteries and devotional practices included kissing. Some of the above could have been the source of the chlorides.

Where enamels are present, the treatment is particularly delicate and labor-intensive because of the friable condition and loss of adhesion of much of the enamel to the under-lying metal. Before enamels are stabilized, overlying debris and adjacent corrosion products have to be removed. This procedure is carefully monitored under the microscope. Some of the enamels have been stabilized with Acryloid B-72, an ethyl methacrylate copolymer, 10% in ethanol with the additon of Cab-O-Sil MS-7 (aerogel silica) as a matting agent.

The objects have been photographed in color slides and photomicrographic slides before, during and after treatment.

Enamelled icons are padded and wrapped in acid free tissue. The objects are stored individually in perforated (for air circulation) polyethylene zip-lock bags with identifying labels. The collection is kept in an environmentally controlled storage room which is monitored periodically and maintains a stable temperature of 68°-70°F. and relative humidity of 50%.

Ethnographic Use

These metal icons were often called "travelling icons" and many were manufactured by the Old Believers of Russia. The Reverend W. Sparrow Simpson wrote in 1867 about 29 similar icons which were brought to England after the Crimean war.

The following is from his paper, p.114:

"The particular kind of portable icon which I now exhibit is in very general use amongst the Russian peasantry. The wealthy classes wear similar icons, but of a much more costly character -- some are even of gold. When a peasant is about to send his son to service in the Army, he often takes from his neck the icon that he and his forefathers have worn, and places it, with his benediction, on the young soldier's breast. To the soldier him-self, the icon becomes a memento because it usually bears the effigy of some Russian saint, very frequently, the patron saint, S. Nicholas; of his family, for this icon may have been an heirloom; of his religion, for

when about to offer his prayers, he opens his triptych or diptych, and kneels before it as a portable altar. He carries it, suspended round his neck, through the vicissitudes of a campaign; and when, his labours ended, he returns to his native parish, he often hangs this cherished possession upon the iconostasis of his village church, as a votive offering to commemorate his preservation."

Old Believers have stated that if the "eyes" of a metal icon are worn smooth, then they no longer use them for devotional purposes. Those metal icons which once were nailed to wooden crosses in cemeteries bear the evidence of nail holes. The above may in part, explain why so many icons found their way into the fair at Nizhni Novgorod where the sale of both new and old goods attracted thousands of people from Russia and Europe every August.

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A THEORY FOR THE DETERIORATION OF A CALCIUM
SULFATE GROUND ON A RUSSIAN ICON

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SUMMARY

The presence of chlorides in a calcium
sulfate ground is theorized to be a factor in
its deterioration.

Introduction

This report is part of a technical study of a
late 18th century Russian icon of the New
Testament Trinity, written by the author in
1981. The observation of this icon in a
controlled and monitored environment provided
an opportunity to record and study unexpected
changes in the consistency of the calcium
sulfate ground.

Physical Construction

The icon measures 26.0 x 30.8 x 2.0 cm. and
is painted in tempera on a flat wooden
support constructed of 3 boards and 2
oppositely-placed transverse slats (shponki).
There is a layer of paper between the support
and the ground and a silver leaf layer is
covered with shellac to appear golden. A
silver-plated brass oklad is no longer
affixed to the icon, but nails previously
driven through it into the panel had caused
the spalling of approximately 6.0 x 9.5 cm.
of the ground. It is this area which was
used for observation and testing.

Grounds of Russian Icons

The grounds of Russian icons were
traditionally prepared from chalk or gypsum
using fish glue made from the swimming
bladders (sounds) of the sturgeon as a
binding medium (Birstein; 1978:1). The
gypsum, often called alabaster in Russian
writings, can be a finely ground calcium
sulfate dihydrate ($CaSO_4.2H_2O$), an anhydrous
calcium sulfate ($CaSO_4$), or a mixture of the
two in any proportion. Both the $CaCO_3$ and
$CaSO_4$ grounds deteriorate under unfavorable
environmental conditions, but the alabaster
ground is more susceptible than the chalk to
crumbling (Filatov; 1961:11).

Analysis of the Ground of the New Testament
Trinity Icon

The ground was initially identified as
calcium sulfate by microchemical testing
using barium chloride.

The structure of the calcium sulfate was
determined by an X-ray diffraction powder
pattern (using Gandolfi 114-6 mm. cameras)
done by Dr. Pete Dunn of the Department of
Mineral Sciences, National Museum of Natural
History, Smithsonian Institution. A sample
of the ground, taken after deterioration had
begun, showed that it was mainly anhydrous
calcium sulfate with some calcium dihydrate
present.

The binding medium was not analyzed, but it is
supposed that sturgeon sound gelatin may have
been the adhesive used in the preparation of
this ground. Determing the exact binding
medium in grounds is a difficult process. In
a study of the amino acid composition of the
binding medias of 5 Russian icon grounds and
the grounds of 5 west European ploychrome
sculptures using a "Hitachi KLA-3B" amino
acid analyzer, the isolation and identification
of the component amino acids could not
distinguish fish gelatin from other aged
animal collagens (Birstein; 1978:4).

Deterioration of the Calcium Sulfate Ground

The icon study was conducted in a large room
where the temperature and relative humidity
were controlled by contemporary heating and
cooling mechanisms.

During the first few days, the ground was
very hard and a sample was removed from the
spalled area by chipping. Five days later, it
was noticed that the ground had changed to the
consistency of firm ice cream and a sample for
analysis by X-ray diffraction was removed from
the same area by scooping. The hygroscopic
calcium sulfate ground appeared to be
absorbing moisture from the environment and
some of the paint layer was lifting. The
wood also appeared to be in movement because
the edges of the shponki on the bare verso
showed a new section of lighter colored wood.

The room was monitored with a calibrated
hygrothermograph (Belfort Instrument Co.,
Baltimore, Md.) which recorded a temperature
range of 67°-76°F. With a relative humidity
of 40-60% in one week. Spot checks of the
environment with a Bacharach sling
psychrometer showed that the temperature and
relative humidity in diverse areas of the room
fluctuated more than that registered by the
hygrothermograph which remained in a fixed
position. Readings in these varied locations
reflected the placement of the heating and
cooling vents, activities of people within
the room and 3 opening and closing doors.

The icon was placed into a microenvironment
made of a polyethylene bag containing an open
dish of silica gel (Tell-Tale Silica Gel
Dessicant, Grade 44; Davison Chemical Co.,
Baltimore, Md.), in an effort to extract the
moisture. The panel was centrally placed and
elevated so that no surface of the
polyethylene was in contact with it and that
the air could circulate freely. Within 2 days
the dessicant had absorbed enough moisture to
change the consistency of the ground from
semi-soft to hard. What was intrinsic in the
$CaSO_4$ ground that made it react so quickly to
fluctuations in the temperature and relative
humidity? The following paragraphs summarize
more extensive research.

Anhydrous Calcium Sulfate, $CaSO_4$

Sometimes referred to as alabaster or
anhydrite, anhydrous calcium sulfate is an
important rock-forming mineral occuring in
sedimentary terranes with gypsum, limestone,
dolomite and salt beds. Anhydrite also
occurs as an accessory mineral in sedimentary
rocks, especially in rock salt (Palache, et
al.; 1951:427). Both anhydrite and gypsum are
associated with salt domes on the northeast
coast of the Caspian Sea as well as in other
areas of the U.S.S.R.. The core of the salt
dome is halite overlain with a cap rock
consisting of limestone, gypsum and
anhydrite; the limestone being on top and the
anhydrite on the bottom (Billings; 1954:257).

Calcium Sulfate Dihydrite, Ca $SO_4.2H_2O$

Known also as gypsum, calcium sulfate
dihydrate is the commonest of the sulfate
minerals. Gypsum converts to anhydrite above
42°C. and the reverse change takes place at
lower temperatures. Gypsum converts to the
metastable hemihydrate in water at about 98°C,
the transition temperature being lowered by
the presence of disolved $NaC1$ or $CaC1_2$.
Commercial plaster of Paris consists
principally of the hemihydrate and is made by
heating gypsum at 190°-200°C.; it often
contains anhydrite or undecomposed gypsum.
Heating gypsum at much higher temperatures
produces anhydrite (deadburned plaster)
(Palache, et al.:1951:484).

Sturgeon Fish Gelatin

The sounds, air bladders or swimming bladders
of sturgeon as they are variously called, are
used in the preparation of a very pure gelatin
used as an adhesive. They consist exclusive-
ly of collagen and are exceptionally free
from other impurities which might be dissolved
upon heating with water. The inner membrane
of fish sounds is the only animal tissue
which consists entirely of collagen (Bogue;
1922:48). When collagen is heated in water
to 80° or 90°C., it is converted slowly into
the protein gelatin, which is an
intramolecular rearrangement of collagen
(Bogue; 1922:50).

Gelatin manufactured from the sounds of
sturgeons is composed of about 49 per cent
carbon, 7 per cent hydrogen and 18 per cent
nitrogen (Bogue; 1922:50). Seventeen amino
acids were isolated from the gelatins of
grounds of Russian icons, with glycine
accounting for 35 per cent of the composition
of gelatin (Birstein; 1978:7). The dipolar
structure of amino acids accounts for their
salt-like properties. Bogue stated that to
free gelatine of all extraneous salts, thin
sheets of gelatin could be suspended in cold
distilled water, changing the water
frequently (Bogue; 1922:61).

A dried swimming bladder was softened in
distilled water and tested positive for
chlorides using the acidified silver nitrate
method. Dried fish gelatin was also positive
for chlorides. This type of gelatin may be
similar to the binding medium used in the
preparation of Russian icon grounds, although
the chloride content may vary according to
the source of the water.

Testing the Ground of the New Testament Trinity Icon

Since alabaster and gypsum are associated
with salt domes in nature, it is possible
that sodium chloride is a contaminant of the
mineral as it may have been mined and used in
the late 18th or early 19th centuries.

The ground of the icon was positive for
chlorides as concluded by testing with
acidified silver nitrate.

Theory for the Deterioration of the Ground of the N.T. Trinity Icon

It is theorized that perhaps an inherent
sodium chloride content in the calcium
sulfate along with the possible addition of
chlorides through a fish glue binding medium,
may be factors in the rapid deterioration of
this alabaster ground.

Since the study was done on only one icon, it
would be helpful to know if any similar
observations or extensive studies have been
made on icons with calcium sulfate grounds.

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ON THE OLD RUSSIAN ICON'S SETTING FRAMES, IN THE CONNECTION WITH THEIR RESTORATION

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SUMMARY

The paper concerns the historical connection of an icon with its setting frame which determines the rational approach to the restoration.

When begining the restoration of the icon covered with a metal setting frame we have to settle the problem of taking off the setting frame or its preserving.
In the past since the artistic value of the Old Russian painting was discovered, the setting frames from the restored icons were removed as usual. In the expositions of the largest museums formed during the current century the icons covered with setting frames are comparatively uncommon. Of course many of these pieces could lose their settings long before the restoration. On the other hand many of these pieces could lose their settings long before the restoration. On the other hand many of collectors prefered to preserve the artistic setting frames on the small "home" icons. Nevertheless the general approach to the problem is quite onvious.
The main reason for removing the setting frames was the care of preservation of the painting as it was believed that the setting frame might cause its destruction. At the same time other considerations had obvious meaning. The point is that the setting frame has marked influence on the general appearance of the piece concealing not only the backgraound but some details, e. g. the inscriptions having important meaning for the attribution of ancient monuments.
Starting from 1918 they began to transfer of the precious setting frames to new supports and later on to keep and show them as an independent work of the applied arts.
For the last 20 years the interest to the ancient icons became much stronger as to the monuments of culture in the very broad meaning of the word. Now they began to preserve setting frames even of the latest origin and of no specific artistic value. There was the belief that the icons with coloured but not gilded backgrounds were already created in the antiquity with the intenti on to adorn them with the metal setting frames.
Such an opinion cannot be admited well-founded due to many reasons.
First of all the coloured backgrounds had the ancient tradition in the Byzantine painting and therefore they were not less canonical than golden ones for the Russian art. As for the metal setting frames they were originally not a si mple adornment, but the precious donation to respected image or temple where it was placed. There were old references of making setting frames where the value of the used material was noted as usual but not the artistical features. Such donations could be done only by the wealthy and they could not concern the common town and country churches. This purpose of setting frames had done impossible their origin simultaneously with paintings. The exceptions took place only with respect to copies of famous icons intended as a present to famed temples and cloisters. In this case the adorning of the just painted icon with a setting frame was determined by its donation aim. The other and very rare exception were the gilded setting frames of copper or iron, which belonged to the time of the decline of the Old Russian art. These are the obvious proof of breaking the traditional medieval ideas.
Thus in the ancient times the great bulk of icons could have neither the gilded backgrounds nor the expensive setting frames.
At the border of 15-16 centuries there begun the movement of so-called "nestyazhateli" (non-grabbers) in the cloisters situated on the left bank of the Volga. Its ideologist Nil Sorsky proclaimed the interdiction of any adorning in the churches and cloisters as well as of their posession of any values. This point of view was not accepted by the official church, but found many followers in the certain social environment up to 19 century. It is evident that the followers could not have icons with setting frames or ones painted on gold.
Thus the setting frames of ancient icons as a rule are the latest addition of more ancient monuments. The problem of their preservation or transfer to another support should be decided according to their relation to the painting.
If there is the ground to believe that the setting frame was made simultaneously with the painting it should be obviously kept in its place. However more often the setting frame distorts the original artistic nature especially on the icons with a coloured background. Not only the detailed study of a monument, but the simple visual perception of it in the original author's version is impossible untill the setting frame is removed. But the setting frame placed on another support and exhibited next to the icon allows easily to imagine its appearance prior to removing the setting frame.
If the setting frame and the painting form a harmonious unity which raises the artistical expessiveness of a monument as a whole, the removing of the setting frame is inexpedient. The same can be said about insignificant icons intended for setting up the museum interiors.

SOME RESULTS OF THE DENDROCHRONOLOGICAL STUDY OF THE ANCIENT RUSSIA ICON AND MONUMENTS OF WOODEN ARCHITECTURE

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SUMMARY

3 boards belonging to 9 icons of Pskov and
Novgorod school of painting of the XIV-XV
centuries from the funds of the Moscow State
Museum of History, carved beards from the ca-
nopy over the Holy Door of the Svjatogorskij
monastry (XIV-XV centuries) and the bars of
the iconostasis of the cathedral of the Vir-
gin's Nativity of the Feropontov monastery
(XV century) were examined by the method of
dendrochronological analysis.
The basic constructive elements of one of
early type of the ancient Russia temples
of the XV century (the church of the Deposi-
tion of the Virgin's Robe at Borodavji of the
Vologodskaja region) were also examined.
As a result the type of the material, the age
of the used wood and the date of the boards
primary utilisation have been ascertained
within a quater of a century.
Building phase chronological characteristic
was obtained and supposition about the date
of the beginning of the buildingap in 1985
was confirmed for the church of the Deposi-
tion of the Virgin's Robe.

For the first time in the USSR in the labora-
tory of the V/O "Sojuzrestavratsija" method
of dendrochronological analyses was applied
for the dating of ancient Russia ikons of
the XIV-XVI centuries and architectural monu-
ments of the XV-XIX centuries.
As a rule butt-end cut of wood is used. In
this case the sequence of tree-rings can be
clearly observed from the core to the exter-
nal part.
Unfortunatly such specimens of building ma-
terials can't be usually obtained. That is
why in practice of the dendrochronological
study of ancient building wood often the cut-
off of the partly preserved wood is used.
In this case the the necessary conditions
are;
1. Safety of tree-ring sequence in the inter-
val not less than 80-100 years.
2. Possibility to observe the annual wood
development at two opposite radii.
3. Safe connection of radii with each other.
Under maintenance of whese conditions planks
of building constructions and the objects of
applied and fine arts can be used for den-
drochronological analyses.

Ancient Russia painting

During the selection of material we proceed-
ded from the following:
1. Only the planks of softwood are suitable
since absolute dendrochronological scales,
existing in East Europe, are constituted for
pine-tree and fir-tree.
2. All the planks should meet the abovesaid
requirements.
3. Art monuments, which are under studing,
should come from the territories for which
tree-ring development regularity is studied
quite enough (that is North and North-West of
East Europe).
4. There is a large set of absolute dated
tree-ring development curves for the said ter-
ritories. This gives a good base for the ab-
solute fixing.

Dendrochronological dating

Herin four works of art of the XIV-XVI centu-
ries will be considered (three ikons and a
carved board from GIM (Moscow).
Ikon "Peter and Paul". Both of the examined
boards are made of pine. The first board (1)
preserved tree-ring sequence for the period
of 160 years at one radius and 122 years at
the other. A core and external rings are not
preserved. However both of the radii are in
good connection with each other. The second
board (2) gives the sequence of 160 rings at
one radius and 102 rings at the other. A core
and external rings are not preserved. The ra-
dii are in safe connection. The examined bo-
ards were made of different trunks.
C_x (index of similarity of the annual develop-

Ikon "Transfiguration". One beard has been
examined. It was made of pine. The rings sequ-
ence of 80 years in preserved at both radii.
There are no core and external rings. The con-
nection between radii is quite close.
Ikon "Paraskeva". Two boards of pine have been
examined. In the first board ring sequence of
100 years is preserved at one radius and 96
years at the other. There are no external and
central rings. The connection between the opp-
osite radii is close.
The second board preserved ring sequence of
100 and 97 years correspondingly. There are no
core and external rings. The opposite radii
are tight-packed.
The examined boards belong to different trunks
which grew in similar conditions. Undex C_x is
68%.
The carved board of pine from Snetogorkij mo-
nastery. Ring sequence preserved with 150
rings at one radius and 77 rings at the other.
There are no external rings. The opposite ra-
dii are tight-packed.

Summary

Summarizing the abovesaid we can make the fol-
lowing conclusion: we have six boards (of
three ikons and carved canopy) pertaining to
the monuments of the XIV-XVI centuries and so
showing the tendency of those time pine ring
development at quite large intervals of 80,
100, 150 and 160 years. This situation gives
us ground to try to make a cross donjugation
of obtained pine-tree ring development curves
and absolute dated curves of dendrochronolo-
gical scales for the XIII-XVI centures for
Novgorod, Pskov and scale for East Europe
tree.
Ikon "Peter and Paul". Development curves re-
vealed the best conjugation with curves for
1359-1535. The development curves for the
trunk of the church of Dormition (1596) which
is situated near Kuritskoje village (Novgorod-
skaja region) and development curves for the
wood of buildings of the XV-XVI centuries
(Pskov cultural layer) were used as basic cur-
ves.
C_x, calculated by means of curves for Novgorod,
were found to be higher then those for Pskov
(53-60% and 50-57% correspondengly). The last
of the preserved rings of the second board
dates from 1535 and that of the first board -
from 1508. Taking into account the difference
in dates for the last rings for the both bo-
ards one can suppose that they were probably
used at the end of the 40-s of the XVI centu-
ry.

Ikon "Transfiguration". As we dispose data
only for one board, and only for the interval
of 80 years, to look for a point of contigui-
ty with basic curves is seemed not to be pos-
sible.
Ikon "Paraskeva". The curves for the wood
from the church of Dormition and foundation
of the refectory of the church of Annunciati-
on in Novgorod (1553) and Pscov buildings
from cultural layer were used.
The best results were obtained at the conjuga-
tion of curves at the interval 1395-1505. C_x
fot the conjugtion with the wood from the
church at Kuritskoje village are 51-66%, for
Pskov curves they are less (50-62%). The last
preserved ring in the second board dates from
1508, and that in the first board - 1505. On
the whole we can most likely date the boards
from the first quater of the XVI century.
The carved board from the canopy of the Sne-
togorskij monastery. Ring development curve
can be situated on the absolute dendrochro-
nological scale in the interval 1277-1425. $C_{x'}$
calculated by the way of comparison with the
curves of the Pskov building wood (XIII-XV
centuries) are 57-60%. The last preserved
ring dates from 1425.
It is a preliminary result. Intentionaly we
didn't consider a number of problems that
scientist faced during planning the work of
this kind. At stating the problem of dating
monuments of applied and painting arts one
have to solve the following problems: deter-
mination of a number of the external rings,
which are not preserved, by correlation of a
number of core rings and external rings.
That will permet to date the felling of a
trunk with calender accuracy. The question of
wood (which was used for making ikon boards
and so on) seasonning time needs a special
consideration.

Wooden architecture monuments.

The church of the Deposition of the Robe is
the unique temple of the Russion North. The
question is to check up the date of its erec-
tion (1485) which is known from the preserved
church papers and confirm, in the case of po-
sitive results, the antiquity of the preser-
ved monument size and its architectural ap-
pearence.
The importance of the correct dating of the
preserved church is, in the first place,
that in this way the possibility of very pro-
longed existance of wooden buildings in natu-
ral contions of North of East Europe is por-
ved. In the second way, the point of view of
historians that the church at Borodavji is
one of the most ancient monuments of Russian
wooden architecture is confirmed.
The church of the Deposition of the Robe re-
presents a few rectangular in plan sizes con-
strained in united frame from the very be-
ginning of its erection. From East to West
are situated: sanctuary, church itself, gal-
lery. The central part (church itself) towers
above the other parts of the building.
The examined collection of specimens is re-
presented in cores except 4 sawn specimens.
It is necessory to mention peculiarity and
complication of the "Kirilovskije" cores.
In the case of examining the cores of Novgo-
rod wood the preservation of the wood was ex-
cellent but in this case splittiness and fri-
ability of wood are observed.
In spite of repeated taking of specimens a
lot of them couldn't be examined.
The specimens were selected off different
rows of logs of the North, South and East
walls of the church central part, refectory.
An interesting tendency is observed which is
the following: in the presence of rings
100 in number, the date of a specimen fluc-
tuates within ±10 ±5 years.
C_x, calculated for this case for 5 synchro-

nous development curves, is 50-60%, that is
quite satisfactory for the examined material.
Preservation of the external rings can't be
quaranteed. Taking this fact into account,
the erection of this church may be dated from
the first part of 80th of the XV century.
That doesn't contradict the church papers but
confirms antiquity of the preserved monument.
The church of the Virgin's Nativity from Pe-
redki (Novgorodskaja region) - one of the
biggest among the preserved cult wooden buil-
dings of the XVI century, though the question
of accurate dating by means of indirect data
causes contradictory opinion of specialists.
It was known from written sources that in
1699 ramshackle by this time building was
subjected to essential repairs: the frame was
sorted out, some details were made again, new
details were added. Later, in the end of the
XIX century, the church was repaired again
and some details were replaced. In 1967 the
monumnet was restored according to the design
by architect L. E. Krasnorechjev owing to
this it has got the appearence similar to an-
cient one.

Dendrochronological dating

Now the church of the Nativity represents a
frame-work, above the central part of which
octagonal frame with marquee is towering.
To the corners between East and South parts
of the crossshaped in plan frame and between
East and West parts side sanctuaries were ad-
joinned.
From South, West and North the building is
rounded by a gallery which is leanning on the
console of the main frame. In West the galle-
ry has a high porch.
The problem of dendrochronological examining
of the church includes ascertaining of the
date of its erection and confirming the date
of rebuilding in the end of the XVII century.
Since there was no scaffolding, a complete
revealling of the original details of the bu-
ilding and architectural-constructive addi-
tions of 1699 was not included in the task.
40 specimens were selected from the different
parts of the building. Samples in the form
of cores were taken by the method of drilling.
Oreservation of the wood is satisfactory. In
some cases the trace of sap-wood are observ-
ed. We succeeded in dating of 26 specimens of
the wood. It was possible to ascertain the
date of felling of trunks (1528-1531) for two
sawn samples.
As a result by the way of comparison with ab-
solute dendrochronological scales for Novgo-
rod and Pskov two chronological bands were
ascertained: 1500-1531 and 1690-1700. It is
necessary to mention the excellent synchro-
nization of the development curves for the
wood of the West branch of the cross, South,
North and central sanctuaries. The most con-
siderable synchronism is observed for the
ring development curves for North and South
sanctuaries and the West branch of the cross.
The latest group of the trunks dates from
90's of the XVII century. That doesn't con-
tradict the time of the rebuilding of this
church in 1699 according to annal's data.
The most ancient group is dated from 20-30's
of the XVI century. This fact confirms the
supposition of L. E. Krasnorechjev about
erection of the church in the first quarter
of the XVI century.

Conclusion

Method of dendrochronological analyses, which
was for the first time applied to date an-
cient Russia ikons and wooden architectural
monuments of Russian North, makes it possib-
le to ascertain the date of the primary usa-
ge of board within a quarter of a century
for the monuments of art of the XIV-XVI cen-
tures. The supposition about building the

church of the Deposition of the Robe in 1485 and the church of the Virgin's Nativity in 30 's of the XVI century is confirmed (the date of its rebuilding is also confirmed).
Thus the possibility of rather prolonged existance of wooden buildings in the natural conditions of North of East Europe has been proved.

Results of dendrochronological analyses of the wood from the church of the Deposition of the Virgin's Robe (Boredavi, Vologodskaja region)

N	Number of log (counted up from a bottom)	Number of tree-rings	Date of a sample
	The main frame		
	South wall		
1	15	88	1478
2	3	86	1474
3	12	80	1470
4	7	64	1472
5	8	142	1475
6	4	106	1480
	East wall		
7	4	210	1481
8	2	195	1481
9	7	103	1481
10	5	148	1480
11	15	127	1474
	North wall		
12	9	151	1481
13	20	130	1478
14	21	85	1472
15	24	104	1480
16	3	76	1472
17	15	71	1475
	Refectory		
18	6 (South wall)	132	1480
19	3 (West wall)	129	1475
20	3 (North wall)	102	1465

Results of dendrochronological analyses of the wood from the church of the Virgin's Nativity (Peredki, Novgorodskaja region)

N	Number of a log (counted up from a bottom)	Number of tree-rings	Date of a sample
	Sanctuary		
	Central part of the sanctuary		
1	10 (East wall)	108	1694
2	11 (East wall)	61	1698
3	6 (South wall)	107	1690
	South part of the sanctuary		
4	7 (East wall)	135	1521
5	6 (East wall)	100	1518
6	8 (East wall)	103	1521
7	13 (East wall)	90	1517
	North part of the sanctuary		
8	7 (East wall)	104	1513
9	8 (East wall)	95	1698
10	9 (East wall)	122	1527
11	8 (North wall)	133	1524
12	7 (North wall)	81	1523
	Cross-shaped frame		
	West branch of the cross		
13	6 (North wall)	113	1512
14	7 (North wall)	64	1507
15	3 (North wall)	125	1513
16	2 (West wall)	79	1507
17	6 (South wall)	104	1511
18	9 (South wall)	105	1500
	North branch of the cross		
19	3 (North wall)	95	1690
20	13 (North wall)	113	1695
21	7 (West wall)	125	1700
22	4 (West wall)	113	1608
	South branch of the cross		
23	6 (East wall)	103	1513
24	2 West wall)	80	1512
	Octagonal frame		
25	1 (East part)	80	1528
26	carrier (of the South side of the gallery)	71	1531

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Section 24

Rock Art

Art rupestre

ETUDE DE PRELEVEMENTS DE PEINTURES RUPESTRES DU TASSILI N'AJJER (ALGERIE)

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RESUME

Lors de deux missions d'étude des problèmes de conservation de l'art rupestre du Tassili N'Ajjer (Algérie), des prélèvements en surface des abris peints du Néolithique ont été effectués. Leur analyse chimique a montré la présence de sulfates sur une mince couche recouvrant les peintures et l'étude stratigraphique a mis en évidence, en général, une seule couche colorée à base d'oxydes de fer (ocre rouge ou ocre jaune) reposant sur la roche.

A la suite d'un séminaire international sur la conservation des oeuvres rupestres du Tassili N'Ajjer (Algérie), organisé conjointement par l'UNESCO et l'Algérie, nous avons effectué, lors de deux missions, une série d'études destinées à cerner l'état dans lequel sont ces peintures. Dans d'autres documents publiés par ailleurs (Actes de la Réunion Internationale sur la Documentation de l'Art Rupestre en région méditerranéenne, Barcelone - Saragosse, 1983), nous avons fait état de nos travaux concernant la connaissance des facteurs climatiques à proximité des peintures ainsi que la surveillance photographique des parois ornées. Il apparaît nécessaire maintenant, pour répondre à la démarche déontologique de la conservation, de mieux connaître la nature des peintures.

1. GENERALITES

Le plateau du Tassili a une altitude de 1200 - 1800 m, et se situe à 25 ° de latitude nord et 8° de longitude est dans le Sahara algérien (Fig. n° 1).
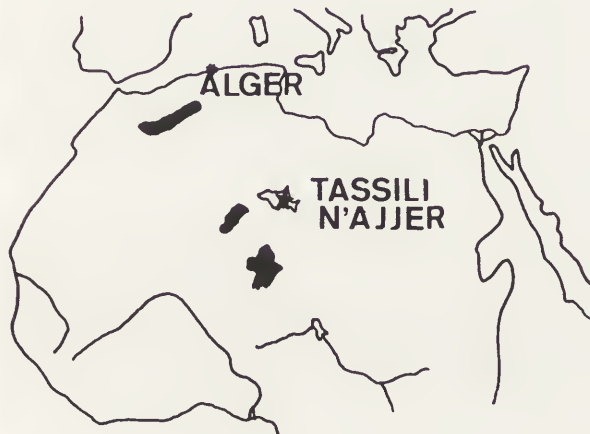
Fig. n° 1 - Localisation du Tassili N'Ajjer (Algérie)

Une partie du plateau, celle où se trouvent la plupart des peintures rupestres, a été désignée Parc National en juillet 1972.

La région est pratiquement sèche toute l'année ; elle ne reçoit qu'une pluie faible et irrégulière -de 25 à 30 mm par an en moyenne-. Les températures diurnes sont élevées, les températures nocturnes sont basses. Parfois la température peut atteindre 40° à l'ombre l'été, le jour, et descendre en-dessous de 0° les nuits d'hiver. Les vents peuvent être violents.

Les peintures -les plus anciennes ont environ 6 000 ans- se trouvent sur les parois de très nombreux abris rupestres ; il en existe encore plusieurs milliers dans la région. Ces abris rupestres ont été creusés à la base de falaises de grès à pic formées probablement sous l'action de l'eau. Dans certains cas, elles ont moins d'un mètre de haut, mais en général elles dépassent la taille de l'homme. Les "plafonds" ont environ 3 mètres de large de sorte que, surtout si les abris se situent le long des gorges, les peintures sont souvent bien protégées, à la fois des vents de sable et des eaux ruisselant des falaises.

Les peintures des abris tassiliens ont subi de nombreuses vicissitudes naturelles dues aux phénomènes de dégradations climatiques et artificielles provoquées par l'action de l'homme (méthode de relevés archéologiques par mouillage des parois, "usage touristique"). Leur aspect a donc été profondément modifié sans que l'on puisse avec certitude affirmer que cela s'est fait dans un sens favorable ou défavorable à la conservation puisque, lors des premiers relevés, toutes les études pouvant nous fournir des renseignements sur l'état des parois au moment de leur découverte, ont été ignorées.

Pour mieux connaître les peintures, indépendamment de la démarche stylistique qui est du ressort de l'archéologue-préhistorien, des prélèvements ont été effectués avec l'accord de l'Office du Parc National du Tassili. Les observations de terrains ont orienté nos travaux dans trois directions :

. Connaissance du dépôt recouvrant l'ensemble des abris

. Etude stratigraphique des prélèvements de pigments

. Identification des constituants chimiques et nature minéralogique.

2. CONNAISSANCE DES DEPOTS RECOUVRANT LES ABRIS

Nous avons regroupé sous le terme dépôt, enduit naturel ou poudre blanchâtre, toutes les microformations en surface des abris peints ; il s'agissait pour nous de répondre aux questions qui nous étaient posées sur le terrain. Nous n'avons pas préjugé des origines diverses pouvant expliquer cette formation, tant il est vrai que la distinction entre action physico-chimique et microbiologique est délicate à établir au niveau des produits d'altération d'un support rocheux étroitement soumis aux facteurs climatiques.

2.1 Localisation et description des prélèvements

. TMZ.82.01 : poussières et encroûtements de la paroi, aspect gris en surface et blanc en cassure, se détachent fréquemment de la paroi. Ce dépôt n'existe pas sur les peintures. Effectué à TIMENZOUZINE

. TMZ.82.05 : croûte en surface dans un abri au nord de TIMENZOUZINE. Couleur beige pâle tirant sur le gris

. TMZ.83.02 : prélèvement de croûtes poussiéreuses beige clair d'aspect argilo-sableux. Localisation dans "l'abri aux Troupeaux" du cirque surélevé (Photo n° 1)

. TMZ.83.03 : même localisation, en ce point la paroi paraît avoir été lessivée ou grattée, des stries sont visibles sur la paroi et sont certainement dues au brossage et au frottage pour faire apparaître les peintures masquées par la poussière (Photo n° 1)

. TMZ.83.07 : croûte de surface soulevée appartenant à "l'abri du Poisson" en rive droite de l'Oued TIMENZOUZINE (Photo n° 2)

. SEF.82.08 : dépôt de paroi de couleur beige au "cirque des Totems" de SEFAR

. SEF.83.15 : croûte blanchâtre partie centrale de l'abri XIII.5.E1 de SEFAR (Photo n° 3).

2.2 Résultats

Les analyses par microchimie, spectrophotométrie infra-rouge au L.R.M.H. et par radio-cristallographie au Laboratoire de Recherche des Musées de France (Monsieur LAHANIER), ont mis en évidence la présence de sulfates, carbonates et silicates.

Exemples d'analyses (résultats du L.R.M.F.) :

TMZ.82.07 - Epsomite de formule $Mg\,SO_4$, $7H_2O$, quartz et $CaCO_3$

TMZ.82.01 - Gypse de formule $CaSO_4$, $2H_2O$

TMZ.82.05 - Gypse + Quartz + Epsomite

TMZ.82.06 - Gypse + Quartz + Epsomite

SEF.82.08 - Anhydrite ($CaSO_4$) + Gypse + Quartz (SiO_2)

Joyce PLESTERS, de la National Gallery, signalait la présence, dans des échantillons ramenés du Tassili par Messieurs MORA et THOMSON en 1974, de sulfates et de quantités négligeables de chlorures et de nitrates.

Ces enduits naturels, qui apparaissent d'une manière ubiquiste aussi bien à TIMENZOUZINE qu'à SEFAR, sites séparés par quatre heures de marche, ne sont pas liés à la présence des peintures. Cette couche a recouvert progressivement les peintures, les cachant ainsi aux premiers archéologues. La genèse en est mal connue, l'apport de poussières éoliennes et le rôle des microorganismes seront des facteurs à prendre en considération.

3. ETUDE STRATIGRAPHIQUE

3.1 Localisation et description

Vingt-neuf prélèvements ont été effectués au niveau des abris à peinture de TIMENZOUZINE et SEFAR ; ils ont fait l'objet d'une étude stratigraphique par l'observation au microscope binoculaire de sections polies. Nous ne ferons figurer ici que les plus représentatifs.

. SEF.82.12 - Abri XII 7 E1, SEFAR : prélèvement de peinture sur le contour d'un grand personnage
La stratigraphie (Photo n° 4) montre :
- une couche blanche dans laquelle nous discernons la forme de grains de quartz, riche en sulfates
- une couche rouge-orangé d'ocre rouge
- une couche brunâtre avec des sulfates

. SEF.83.19 - abri XIII 4 D1, SEFAR : prélèvement de couleur jaune sur la partie sommitale du personnage (Photo n° 5)
L'étude stratigraphique -de la roche vers la surface- (Photo n° 6) montre :
- une couche avec des gros cristaux blancs (grains de quartz) contenant des carbonates et des traces de sulfates
- une couche jaune constituée d'ocre jaune

. SEF.83.13 - abri XIII 5 E1, SEFAR : prélèvement de peinture d'un mouflon de couleur jaune-brun (Photo n° 7)
L'étude stratigraphique (Photo n° 8) indique :

- une couche épaisse blanche avec des cristaux blancs où l'analyse révèle la présence de carbonates et de traces de sulfates mêlés aux grains de quartz
- puis une couche jaune riche de "cristaux" rouges et noirs ; il s'agit d'ocre jaune et d'ocre rouge ; l'oxyde peut prendre, quand il est en micronodule, un aspect noirâtre.

. TMZ.82.04 - localisation à TIMENZOUZINE, lieu-dit "Abri aux troupeaux" du cirque surélevé : petite écaille rouge sur la peinture d'un bovidé (Photo n° 9)
Ce prélèvement possède une stratigraphie plus compliquée et nous remarquerons (Photo n° 10) :
- une couche jaunâtre constituée de grains de quartz
- une couche blanche avec des grains de quartz
- une couche grise avec des particules très sombres identifiées comme du noir animal
- une couche rouge-orangé d'ocre rouge avec des petits points d'ocre plus concentré et plus foncé
- une couche brunâtre

. SEF.82.16 - "Abri du Dieu pêcheur", SEFAR : prélèvement au niveau du trait épais de couleur rouge sur la patte postérieure d'un bubale (Photo n° 11). La stratigraphie (Photo n° 12) révèle :
- une couche blanche épaisse où l'on distingue la morphologie des grains de quartz cimentés entre eux ; cette couche est riche en sulfates
- une couche rouge-brunâtre d'ocre rouge
- une fine couche brunâtre avec des sulfates

3.2 Résultats

Nos observations permettent de reconstituer un modèle simple de stratigraphie picturale ; de la roche mère saine vers l'extérieur nous distinguerons :
- le grès avec des grains de quartz liés d'un ciment siliceux
- une couche d'altération du grès riche en sulfates
- une couche de pigment
- et une nouvelle couche riche en sulfates et de micro-grains de quartz

Autour de ce modèle, des variations peuvent exister avec, notamment, la présence de noir animal, mais le nombre général des échantillons prélevés et celui où cette "anomalie" est notée, sont trop faibles pour tirer des conclusions en rapport avec le style de ces peintures.

Un phénomène intéressant est la constitution sur les peintures, après leur application, d'un nouveau dépôt riche en sulfates, décrit au paragraphe 2 de ce document. Il conviendra de mieux comprendre sa genèse, le rôle des facteurs altéragènes évoqués dans une autre communication (J. VOUVE et J. BRUNET) de ce congrès et de prendre en considération le rôle de l'eau (infiltrations, ruissellements), les apports éoliens de poussières, le rôle des microorganismes. Dans ce sujet tout n'a pas été dit et d'autres chercheurs comme François SOLEILHAVOUP y travaille.

Nous n'avons pas eu la chance de faire des prélèvements sur des parois ornées vierges de toute intervention ; pour faire apparaître les peintures masquées par ces dépôts, les interventions antérieures pour faire les relevés, ont du être rudes à l'aide de brosse et en humidifiant la surface. L'étude d'abris intacts prend donc maintenant un grand intérêt ; souhaitons qu'elle puisse être réalisée.

4. IDENTIFICATION DES CONSTITUANTS CHIMIQUES DES PIGMENTS

La détermination minéralogique des échantillons DJA.82.18 -plaquette de schiste rouge-, TMZ.82.03 -plaquette de schiste rouge ramassée dans l'Oued TIMENZOUZINE- et TMT.82.17 -schiste jaune provenant de ISSAOUALAFEN- a été réalisée à l'aide de la diffraction X et de micro-fluorescence X.

Les échantillons DJA.82.18 et TMZ.82.03 contiennent de l'hématite, oxyde de fer responsable de la coloration rouge du schiste ; TMT.82.17 contient de la goethite, responsable de la couleur jaune.

L'examen de diagrammes par spectro-photométrie infra-rouge a mis en évidence la présence de nitrates, d'oxalates et de sulfates ; nous ne mentionnerons que les diagrammes les plus représentatifs :

. TMZ.82.05, avec oxalates, nitrates et sulfates (Fig. n° 2)
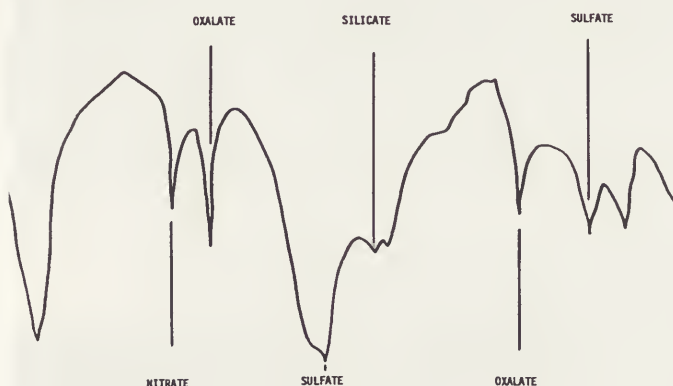
. TMZ.83.07, avec carbonates, nitrates, sulfates (Fig.n° 3)
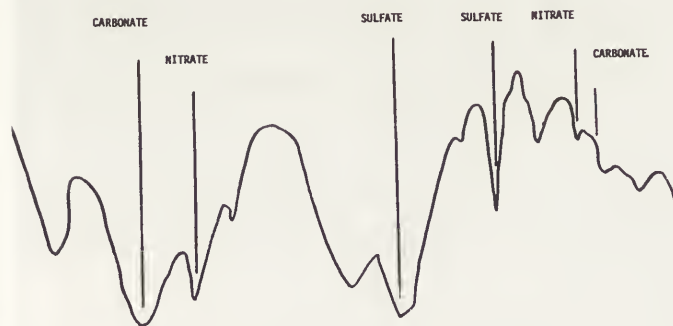
Oxalates et nitrates témoignent d'une activité organique au niveau des parois et de nombreuses hypothèses sont à faire pour justifier leur présence.

CONCLUSION

Nous venons de voir ce qu'une étude chimique et l'observation en laboratoire de prélèvements pouvaient apporter comme données pour la conservation. Le travail d'analyse n'est pas fini et il y a de nombreux sites du TASSILI sur lesquels nous ne possédons rien. Pour comprendre l'état actuel des peintures, il faudra reconstituer tous les processus d'évolution qui ont pu exister depuis le Néolithique ; l'étude des états de parois ornées devrait le permettre.

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Photo n° 1
Localisation des prélèvements TMZ.83.02 et TMZ.83.03

Photo n° 2
Localisation du prélèvement TMZ.83.07
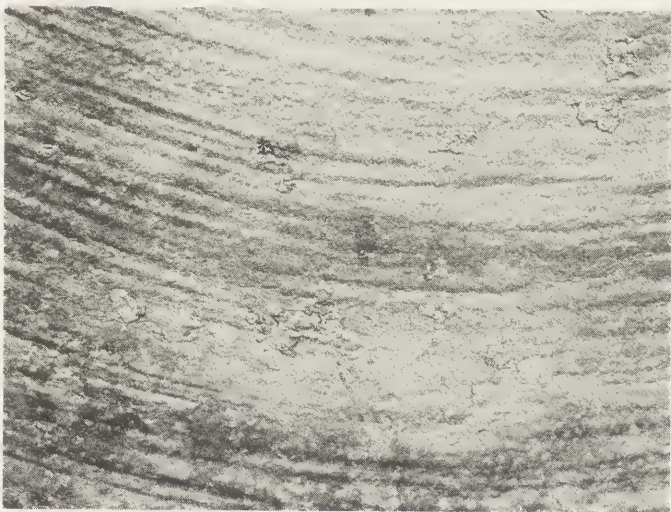
Photo n° 3
Localisation du prélèvement SEF.83.15
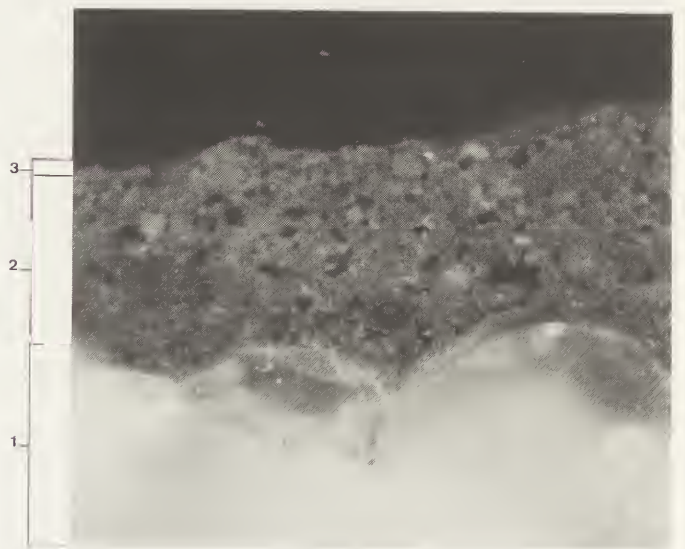
Photo n° 4
Coupe stratigraphique de SEF.82.12
1 : couche blanche (quartz)
2 : couche rouge-orangé (ocre rouge)
3 : couche brunâtre (sulfate de calcium)

Photo n° 5
Localisation du prélèvement SEF.83.19

Photo n° 6
Coupe stratigraphique de SEF.83.19
1 : couche blanche (quartz + carbonate + sulfate)
2 : couche jaune (ocre jaune)
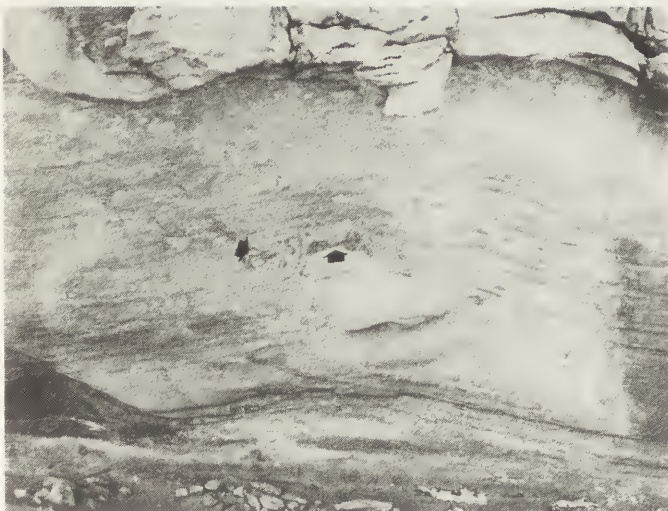
Photo n° 7
Localisation du prélèvement SEF.83.13
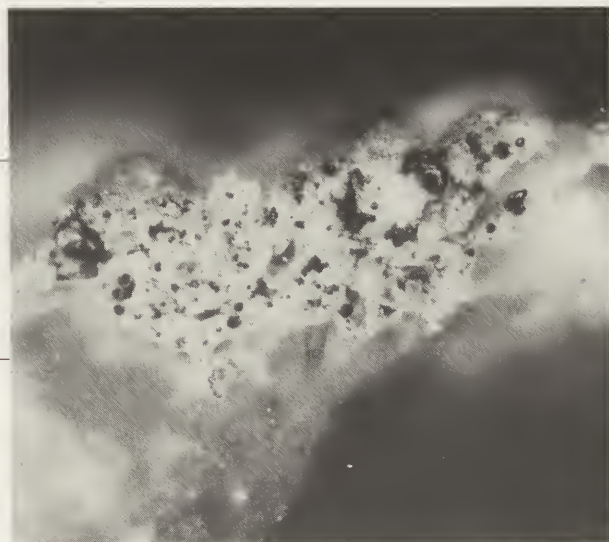
Photo n° 8
Coupe stratigraphique de SEF.83.13
1 : couche blanche (quartz)
2 : couche jaune (ocre jaune + ocre rouge)

Photo n° 9
Localisation du prélèvement TMZ.82.04
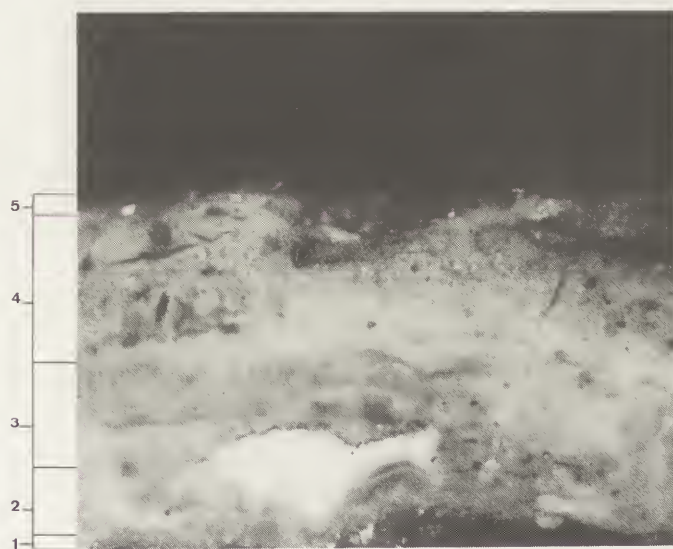
Photo n° 10
Coupe stratigraphique de TMZ.82.04
1 : couche jaunâtre (quartz + sulfate)
2 : couche blanche (quartz)
3 : couche grise (avec noir animal)
4 : couche orangée (ocre rouge)
5 : couche brunâtre (sulfate)
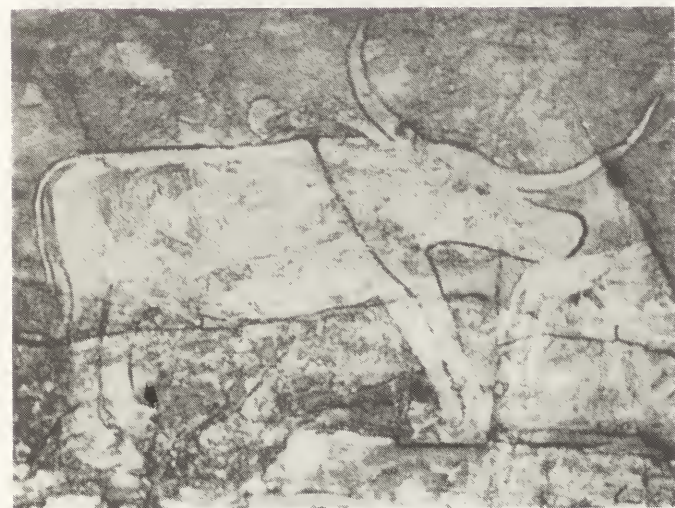
Photo n° 11
Localisation du prélèvement SEF.82.16

Photo n° 12
Coupe stratigraphique de SEF.82.16
1 : couche blanche (quartz)
2 : couche rouge-orangé (ocre rouge)
3 : couche brunâtre (sulfate)

DECAY AND STONE TREATMENT IN THE HIGH ANDES OF THE SOUTHERN REGION

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Metereological action on rocks and old hewn stone in the High Andes mountain range region with dissimilar climatic conditions are analysed. An experience carried out at more than 3.000 m. (above sea level), in sites 200 km. away from each other, show the open weather disparity of effects and poses a dilemma regarding their causes of decay. Reasons for disintegration are analysed and some operations to be made or started at the archeological site itself are suggested. Treatments carried out deal with the cleaning methods through doughs which retain dirt without rubbing the pieces. Washing : the criteria followed is not to inmerse violently or over long periods of time a piece weakened by salting in a permeable consolidant, but to extract soluble elements before any consolidation process. To accomplish such procedure with minimal risks a safe "basket" prop is suggested. Concluding, bonding of broken rocks depend fundamentally on structural conditions, state, and size of them. A specific classification on the matter was made stating the adhesives tried out by the Instituto Técnico de Restauración on the sites.

In the mountain range region there is a lack of work dedicated to the exhaustive study of its archeological values related to the rocks and especially to the caves and caverns which sheltered the pre - hispanic ethnic groups. Due to large distances and transport problems over treacherous ground in the area, very few scientists and geologists have done team work to analyze the situation. The proof is in the loss of material, (which simply disintegrates when extracted) due to lack of immediate intervention by specialized conservation technicians who were never consulted in these cases.

At many sites and in hundreds of caves, really interesting simple signs, drawings or ideological incisions can be seen. Some have been damaged by the lay - man and many even by the same scientists. It is important to educate the tourist and climber who are inclined to damage the archeological pieces or build fires inside the grottos, caves, or pre-hispanic shelters. Even the scientist is to blame for, often when taking photographs of the pictography, the carvings or petroglyphs of little contrast, they use chalk or other elements and the rough surfaces retain the particles forever. Not one of the sites in the mountain region mentioned is guarded, and as a result is easy prey for unscrupulous people.

The natural deterioration of the hewn stone consists in the logical degradation just by being exposed to the inclement weather over the centuries. Consequently many traces are disappearing or have completely disappeared. Many of the sites can only be reached by mule, which is a problem in itself and add to this the lack of organized planning. That is to say the interdisciplinary character of any scientific work is disregarded. To justify the methods which are going to be described it is necessary to take into account the diverse climatic conditions. These, if unknown, will hinder the complete understanding of the problem.

The Andean system, one of the four distinguishable in the Argentine territory, is a region of high mountains and very arid plateaus covering the Central Andes and Puna, and from the Tropic of Capricorn to the 40 th. southern parallel. It includes peaks like the Aconcagua (7.035 m.) and the Tupungato (6.800 m.). There are two main kinds of winds, the ones from the Pacific and others from the Arctic. The Pacific winds, advantageous to Chile, reach the area from the west at which point they are cold, dry and sometimes of hurricane force which cause the aridness of the plateaus. Especially in summer the Pacific winds reach the area of the prevailing Atlantic ones, due to the formation of cyclones over the Central Plains. Amongst these winds, the "Pampero", brings humidity condensation in moderate rainfalls and heavy electric storms. When the pressure stabilizes and the atmosphere clears the weather turns to normal, like this the front moves north covering the whole country and reaches Uruguay, southern Brazil and Matto Grosso. The Antartic winds reach the area of the prevailing Pacific winds (polar wave), mainly in winter (sometimes in other seasons) causing the deplacement of air, the masses of the Pacific and the Atlantic and their common front. The Polar air penetrates the Patagonia mountain region and southern Pampa bringing snowfalls and freezing in winter and rain in summer, and changing the Polar front to 35° S.

The average temperatures of the high peaks is about - 16°C and due to the clear skies the sun is very intense; even though there are very few registers it is calculated that the temperature is below zero all year. Also characteristic of this region are the powderized snow storms (called white wind) and heavy snow - falls. Up top the winds, which are limited and defined by the valleys and ravines, are violent, permanent almost during the day, variable and sometimes blow in the opposite direction of the passing clouds. For example, the "Zonda", a typical mountain wind which comprises the region we are dealing with (Northern Cuyo) is classified as "Fohen" a wind falling from the heights. It is dry and brings with it, deep physical and psychological con-

sequences.

The Mountain Valleys

Normally in the deep valleys there are torrential
rivers which, when temperature drops give off the accu-
mulated vapour which in turn changes to snow or ice
and these are then carried further by the wind. During
autumn and winter the lower regions are under a layer
of snow between 30 cm. and 90 cm. in depth and which is
even deeper in the surrounding hills.

The above mentioned meteorological conditions show
undoubtedly that there are four sources of deteriora-
tion:

    a) Freezing
    b) Erosion
    c) Decomposition
    d) Organic Activity

a) Freezing: it is a fact that in deterioration of rock
due to freezing, different physicochemical factors play
a part. These should be individually and carefully stu-
died and point out clearly the safe intervention for
its protection, if an exact solution is to be found.

Basically it is not just the large pored rocks which
are the most affected by the oversized action produced
by a change in water's state, but in some variegated ,
fine grained rocks the forces operate in each cell. The-
se forces concentrate on the walls and as they are not
permeable do not allow for expansion, which causes mi -
crofisures and finally disintegration. This usually
occurs with the help of other physical factors.

Frequently obsidian is found in the archeological
material of this region, usually in the form of arrow-
heads, which respond to an almost universal morphology.
Also to be found are a number of pieces in pomice who-
se composition is the same as obsidian (that is silica,
feldspar, potash, or soda and abundant water). Pomice
stone is more porous and its specific weight is 0.9
(allowing it to float). Even though the morphologic
structure of both materials is completely different ,
they are both equally resistant to ice- compression .

b) Erosion: The destruction of rocks by disintegration.
Generally this is due to the strong lashing winds,
which in turn carry detritus of the original rock in a
constant horizontal shower. This phenomenon is not as
simple as it seems. A number of factors intervene which
are difficult to be precise about. Some of these being
natural decomposition of the original components, li-
ving organisms, the effect of ice, and through nitrate
secretions of animal origin.

The complexity of the phenomenon which work together
are shown in an experiment carried out at two sites less
than 200 km. apart. There, identical samples of: recen-
tly hewn crystallized hemitropic laminar marble, saccha-
roid plaster, ordovician or cambric calcareous creta -
ceous sandstone were left out in the open. The sites in
question were San Bartolo Peak (1) of 3.200m. and the
Pelado Peak of 3.420 m. and the results obtained were

the following:

- - - - - - - - - - LAMINAR MARBLE OF HEMITROPIC CRISTALLIZATION
- - - - - - - - - - SACCHAROID STRUCTURED PLASTER
- - - - - - - - - - ORDOVIC OR CAMBRIC COMPACT CALCAREOUS
- - - - - - - - - - CRETACEOUS SANDSTONE
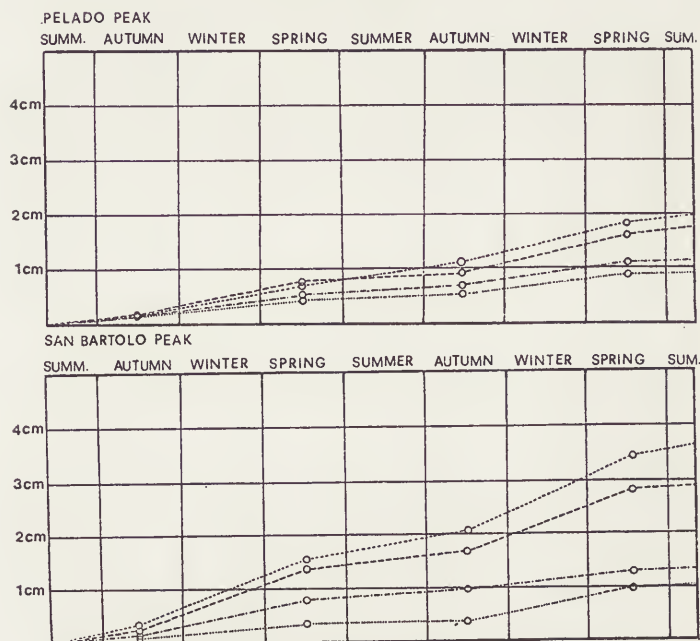
Loss of thickness in recently hewn stone in a period
of two years.

Instead of giving us a logical answer the results
are inclined to put forward more questions which are
impossible to answer without guessing. Any hypothesis
could be risked because the Pelado is in an area domi-
nated by calcareous and graywacke. While the San Barto-
lo is surrounded by metaliferrous ground and near - by
there are many iron-bearing formations which produce
considerable electric charges. The storms in this area
are charged with electricity and full of sparks which
are discharged over the high peaks.

c) Decomposition: due to natural changes there are many
rocks which are likely to disappear in the near future.
The atmosphere is one of the epigenetic agents which
mainly interferes in the rocks' decomposition. Its action
is extremely complex and it is made up of complicated
factors resulting from the help of electrical phenomenons,
chemical ones due to the elements in the air and aided
by the humidity in some cases. Also the phenomenons cau-
sed by uneven temperature peaks. All of them converge in
one: the action of open weather.

The chemical action on the rocks' minerals reaches a
point that it determines their loss of coherence and
they end up disintegrating. This phenomenon is abetted
by the humidity in the atmosphere which hydrates diffe -
rent minerals converting them in earthy or sandy masses.
The air's oxygen, oxidizes the minerals and the rocks
become easily separable. Also the carbon anhydride com-
bined with the humidity increases its dissolving rate
and some affected rocks decay completely.

The feldspars of granite, sienite, trachyte, and dio-
rite disintegrate due to the action of carbonic acid
which produces a loose mass, kaolin, which in turn con-
tains iron-bearing elements which are the results of the

transformation suffered in unison by the micas. Especially the sodium – calcium diorite's feldspar sometimes suffers a transformation in volume which not only affects the surfaces but changes the whole mass of the blocks.

d) Organic Activity : On the medium and high mountains the vegetation problem is not very serious. In some troglodytic caves though, bromeliaceaus plants concentrate and multiply, damaging the decorated walls with their roots but these are easy to eliminate. The biggest problem which affects the shelters is the accumulation of organic detritus and animal alike. This is due to the presence of bats, foxes and other species over the centuries and creates a nitrous atmosphere which permanently deteriorates the drawings and petroglyphs inside the caves. It should be pointed out that often between the overlapping stones a kind of mortar is to be found. This is a manure amalgam of the small rodents. It is like vitreous dross and is highly resistant. These materials, along with the soft earth and ashy remains, which have a strong smell of ammonia because of the animal debris, add to the destruction.

Generally when trying to check the rocks' decomposition process or other spoilt objects, especially in very deteriorated archeological ones, the main condition is left aside: restoration reversibility. This occurs when pieces of diverse materials (stone, wood, bone, etc) are put to soak with the intention of consolidating them. Sometimes these interventions are not fully justifiable. Something similar happens in the cleaning of these objects. Often they are harshly treated due to either their weight or a certain carelesness that seems a common practice in specific rock treatment centers. The rubbing of pieces either with cloth or brushes is quite usual in laboratories , which can give the surface a different look. Another problem is the identification numbers applied to the objects that eventually demerit them. Excesses of this kind, which are quite common, have to be gotten rid of, and milder methods used in their place.

The following are some of the techniques used in the treatment of rocks concerning:

1) Cleaning
2) Washing
3) Extraction of Salts
4) Mounting of broken pieces
5) Consolidation

1) Cleaning : There has to be a limit in the cleaning of antique pieces because often the patina is mistaken for dirt accumulated over the years. To day it is more and more difficult to know when to stop due to the number of products and methods in existence for this purpose. False patinas can often be seen on museum pieces due to rubbing, brushing or even dirty hands and these can be more difficult to remove than the ones caused by time itself, which are usually harmless.

Before starting on the preliminary treatment of the lithic works in the Andes it is important to know that the water in the area is very hard. This is not only characteristic to the nearby towns and villages. But to a wide belt the length of the range. So, when pieces have to be cleaned it is necessary to use de – ionized water because natural water due to its high content in iron and other materials could damage the constitution of the same rocks. Due to the bulk of some pieces, they are not in showcases and are liable to get dirty and even the smaller ones in cases suffer too, but to a lesser extent. As a result, periodical cleaning is required because the accumulated dirt can cause a slow relentless deterioration. It should be considered though, that the constant use of cloths, brushes and other cleaning tools, leave their mark on the object's surfaces.

To carry out this work a sort of hard mixture of wheat flour and water can be prepared and to which small quantities of ammonia can be added, depending on the technician's criteria, as the proportions vary according to the needs. Also it has to be taken into account that in some rocks that have iron pyrites, chalcopyrite, or other oxidizable materials, it is not convenient to use ammonia due to its easy oxidation.

Once the dough has lost its initial sticky stage, it can be applied with the palms using light pressure. Thus the dirt and dust stick to it. The dough should not be compressed excessively as some particles could stick to it. With this method the old chalk applied to the petroglyphs can be removed. Heavier dirt can be removed by using quick setting silicone rubber. Once the components- -latex and catalyzer- are mixed, they are applied to the surfaces in thin layers. Once the latex hardens, it can be peeled off, taking the dirt with it.

2) Washing: As in the preliminary treatment de-ionized water is used for washing and extraction of salts, particularly if prolonged soaking, a risky alternative, is required.

In the case of well preserved pieces washing is simple, hence a neutral soap as tensioactive can be used according to the conservator's criteria. After washing some sort of stains are difficult to remove.

Rocks found in caves or sites with high nitrate content debris have characteristic stains. These are in the form of rings at different levels which encircle the pieces. Evidently these stains are produced by filtering where there are alternate layers of accumulated ash and animal secretions in the ground. They remain after washing and are difficult to remove even using active solvents. This is because the dirt has filtered through even in the most compact rocks (jasper, basalt, diorite, etc.) Obviously the absorbent ones are more affected (all sedimentary and volcanic tuffs, pomice, gneiss, micose, slate, etc).

Rocks which had been damaged were treated successfully with locally applied D.M.F.[*]

[*] (Dimethylformamide: Important organic material solvent. Water miscible, excellent dosage action. Residues aliminated once applied.Its vapours act as solvent too. Dangerous poison, if inhaled symptoms are irreversible.Also

poisonous to skin osmosis.) The deep action of this product softens the residues absorbed through the pores and usually one application is enough. However in some cases other solvents are needed to remove them.

3) Extraction of Salts: To extract the salts the pieces are submerged for set periods in hot, or cold baths and sometimes alternating the temperatures if required . In this work one of the main problems to point out is the need to protect the wholeness of the surfaces (pictorial layers, gildings, substrates and fissures about to ex - plode) because generally the salts have produced serious disorders in the particles and fragments of which the rocks are made.

A two-stage prop can be made to protect the surfaces and prevent loosening without obstructing the permeabi- lity, a condition "sine qua non" in the dissolving and extraction of salts. First put a piece of tissue paper or the like on the rock, then with a soft brush apply the adhesive which should transpose and adhere to it. Without leaving any spaces apply another piece of paper and so on until the rock is covered. Sometimes, when the surface allows, the adhesive can be applied directly and then adapt the paper. The adhesive can be prepared using methylcellulose and water and made up to the density required. In most cases the proportions used were:

Water................................... 100 c.c.
Methylcellulose...................... 10 g.
This gives a thickish paste.

Before continuing one should ensure that the rock is completely covered and the tissue paper is totally dry. This operation in some cases can be carried out at the site enabling the object to be transported without fur - ther disintegration. When the paper dries it girds the surface keeping loose particles in place and even putting them back if flaking occurs.

It should be pointed out that the salts are inclined to produce an expansive effect and that is why generally the affected parts are found above level. As the paper dries out, it produces great tensions especially on this parts.

The second stage of the prop is for the laboratory. It consists in applying a piece of very loose medicinal gauze on the paper. This gauze is saturated in a harde- ner which resists prolonged soakings. This implies a to- tal imbibition preferably carried out in vacuum.

The consolidation which can be used are epoxi - re- sins for short soakings and poliester ones for longer periods or when thermal protection is necessary in hot baths.

How to use: The saturated gauze is wrung out and applied to half the piece. There should be enough mate- rial left over at the edges to simplify the task and it should not be pulled too tight. One should be extremely precautious not to move it once set on the object, as it would make the tissue paper water - proof. Then fix a sheet of thin polyethylene and on top of that a layer of clay, thick enough that its weight adapts the gauze to the surface. The clay should cover more than half to

give a better hold to the prop. The object should remain in this state till the resin hardens. Then, the clay and polyethylene are removed and the edges trimmed. The rock is then turned over and the same procedure repeated. Fi- nal touches may be needed at the joints or concave parts. Taking care not to touch the tissue this can be done by applying the same resin to the gauze either with a fine brush or a piece of card-board coated thinly with resin, taking great care not to impregnate the tissue. Depen - ding on the pressure the prop could exert the build - up of resin can be repeated. Like this the rock can be soa- ked without fear of disintegration and exposed to pro - longed washing even in highly agitated water.

Removal of the prop: once proven that there are no more salts left in the washing water the object is left to dry. Then proceed to cut the gauze. The tissue re - mains on the piece but it is not stuck and it should be removed systematically taking care that there are no lo- sses. The presence of the tissue allows any loose parti- cles to be fixed in place.

Conservation is an interdisciplinary task "par exce - llence" and it should be taken into account that this technique was used successfully on ceramics *   , even when it was the exterior parts that were affected.

4) Mounting of broken pieces: A broken rock carving of archeological value which needs mounting should involve the same effort as the one made when restoring a painter's most precious work. This requires a purely conservative criterion. It should be taken into account that the con- tact of a fracture may be the only means to study the composition material of an object thoroughly; even more so, the complex structure of a rock. Thus, a sad accident may lead to a highly useful observation. But, what ha - ppens when the fractures become useless due to retentions and saturations in the piece ? In these conditions, it will be impossible to reveal part of the intimate struc- ture, and it will be difficult to infer the way the rock or mineral was formed.

To approach this kind of intervention, we should first consider the possibility of employing a purist criterion, holding the piece with an external metal or acrilic prop which should be able to keep the pieces in place; its strength should depend on the weight and size of the work. Thus, any adhesive which adulterates the contacts can be completely eliminated. Such operations on archeological pieces are generally understood by any museum goer. Pie- ces of brittle constitution should be bonded with adhe- sives as an operation of the type above mentioned may da- mage their edges.

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* In the case of ceramics, they were covered externally as previously explained; then they were kept with water inside them, alternating this procedures with total im- mersion.Thus, when, full of liquid they are taken out of the bath, salts crystallize on the surface due to evapo- ration and on soaking them back these crystals dissolve in water.

When it is necessary to use adhesives, they should be carefully selected, bearing in mind not only the size and weight of the work, but also its fracture characteristics. It is important to know the interrelation between fractures and adhesives, according to the following types:

Compact
Saccharoidal
Laminar
Earthy
Conglomerate
Absorbent
Highly Porous
Vitreous

<u>Compact:</u> Compact fractures are typical of coherent rocks -in which the component parts are joined together - that is to say that their mineralogical elements are coetaneous. We can mention some granitic examples such as granite, trachyte, andesite, porphyry, gabro, diorite, syenite, diabase, etc. Among other types of rocks with these characteristics, there are some quartziferous stratum onos like the gneiss and the graywacke. Special attention should bo granted to the graywacke and the basalt, since their fractures (conchoidal in the case of some basalts) offer less physical retention to adhesives. Some very compact calcareous ones also present conchoidal granulous fractures, and they should be included in this group, as well as the dolomites.

Small pieces	They can be mounted using a mixture of P.V.A. and methylcellulose*.
Medium-sized pieces	They can be fixed with P.V.A. and methylcellulose 4 - 1
Big pieces	Epoxy resins may be usod.
Very big pieces	It is advisable to use adequately loaded epoxy resins. Sometimes it is necessary to use props or internal dowels sealed with poliester resins.

<u>Saccharoidal:</u> This kind of fracture takes place in dissimilar rocks regarding their hardness, such as alabaster, marble and plaster. Similar surfaces can be found in quartzites, sandstones and dolomites.

Small pieces of loose fracture	They can be bonded with sandarac varnish dissolved in alcohol. The adhesive is applied on both surfaces, and once dry, the surfaces are damped again and both parts are pressed together until they dry out.
Medium sized pieces	They can be mounted with P.V.A., to which different amounts of skim condensed milk are added.
Big pieces	An adhesive can be prepared with: Water..................... 1400 c.c. Bone glue................. 130 g.

* In every case, it was prepared as follows:
Water........................... 100 c.c.
Methylcellulose .... 10 g.

Big pieces	Plaster of Paris .... 50 g. 96° Alcohol.................... 100 c.c. It should be applied hot and the surfaces to be bonded should be previously heated with a hair-dryer .
Very big pieces	It is recommended to use internal stainless steel dowels.

<u>Laminar:</u> It is typical of many metamorphic rocks such as steatite, asbestos, crystalline slates, schists, mica schists, micacoous gneiss, etc.

Regarding their hardness they are a heterogeneous group; however their common characteristic is the low absorption of their surfaces and a great physical retention capacity.

Small pieces	They are easily assembled with a mixture of methylcellulose 50% and P.V.A. 50%. (Methylcellulose was prepared as indicated above).
Medium - sized pieces	According to their weight and characteristics, they can be bonded with P.V.A.
Big pieces	They are generally assembled with epoxy resins.

<u>Earthy:</u> In the mountain range region few archeological rock pieces present this kind of fracture. It is common in decomposing materials such as certain sandstones, trachytes, and diorites, in which their leucocrats materials disintegrate into earthy materials.

In some ferruginous silex objects (petrosilex with oligist) also in quartzes of the same kind found in a set site there is an oxidation that pulverizes some areas and transforms them into weakened earthy ones which break easily. There are abundant archeological pieces made of phyllite, some of whose decompositions in talc or talcous materials produce clastic fractures. Some marbles and other calcaerous rocks, may, at times, present pulverizing surfaces. Earthy surfaces are extremely difficult to bond because of their inconsistent structure. They require adhesives that filter readily, and their contacts generally need a persistent saturation before the final coupling.

Small pieces	They can be mounted with a mixture of paste and glue in suitable proportions In order to get a good mixture, the paste should be quite dense, its fecula perfectly cooked, and the gelatine a bit more liquid. The pieces can be previously consolidated as explained below.
Medium - sized pieces	They can be bonded with P.V.A. and a third part of methylcellulose prepared as indicated. It is often necessary to strengthen them previously by means of a mixture of P.V.P. (polyvinylpyrrolidone) and alcohol, or a P.V.A. solution of 5% to 10% in toluene. The mixture is prepared as follows

Big pieces
{
Alcohol .... 75 c.c.

P.V.P. .... 10 g.

Epoxi resins can be used for impregnation and they can be loaded for a better coupling. If necessary, the pieces may be consolidated as explained above.
}

Conglomerate: Conglomerate fractures belong to three types: compact conglomerates, breccia, and loose conglomerates. The compact ones have a strong cement material and it differs from gravel in its hardness. The breccias have similar hardness in their cement and aglomerate stones. Some of them are volcanic in origin (aglomerates), their fractures are similar , and they can be treated in the same way as the granitic contacts seen in the first type.

As regards loose conglomerates, they frequently demand the same treatments as earthy fracture rocks. Conglomerate fractures are likely to have good physical retention if their components are firm; therefore, in general, aqueous adhesives can be successfully used even for big pieces.

Medium – sized pieces { P.V.A. conveniently dispersed in water

Big pieces { Lime casein adhesives can be used.

Absorbent: These fractures are typical of calcareous tuffs. There are also some pieces made of amianthus, in which the contacts are relatively absorbent according to their type and state. These joints are subject to surface absorption degree, therefore it is necessary an adequate handling of the adhesive. The parts to be joined are soaked, and once dry, they are pasted again and held together till they finally got dry. In the case of huge pieces, they generally require adhesives which are difficult to remove once set.

Small pieces { They can be bonded with P.V.A. and methylcellulose 3 – 1

Medium – sized pieces { They can be assembled with eposi resins.

Highly porous: In spite of their porousness, these pieces do not present clastic disintegration; on the contrary their fractures are firm and retentive. Volcanic tuffs and pumice stones belong to this group. The latter have been extensively used to make several utensils all along the mountain range region.

Small and medium sized pieces { They can be mounted with epoxy resins Surfaces needn't be excessively soaked.

Vitreous : This kind of fracture is frequently found in many small cutting objects, though they are made of different kinds of rocks. However considering their conservation, it would be useful to classify them considering their morphology: conchoidal and flat; and subdivide them according to their surfaces shine and polish, into glassy, waxy and resinous.

Conchoidal: they are surfaces in the form of convex and concave shells, which somehow allows a better physical retention. The most frequent rocks are: obsidian, petrosilex, opal, jasper, chalcedony, etc. In some cases, particularly in quartzes, some wavy or grooved forms make the bonding more retentive. This happens with the flint stone (silex), which quite often presents splintery fractures.

Flat: they present horny silex; some basaltic lavas and other rocks which belong to the hypercrystalline group of the syenites like the trachyte, used for making arrowheads by most of the region's cultures.

Small Objects {
Conchoidal waxen or resinous and hypercrystalline flat fractures { In general, cyanocrilates join their surfaces very well.

Conchoidal, vitreous and smooth flat surfaces { Suitable epoxi resins adequately loaded can be used.
}

Other types of fractures

The above classification does not pretend to be perfect. It would be impossible to deal with all the problems that may arise new enigmas, since the same material may present different difficulties. The calcareous ones, for instance, present the following types of fractures : compact and conchoidal as in limestones; granular as in microcrystalline marbles; saccharoidal as in marbles and alabasters; conglomerate as in breccia marbles; earthy as in chalky lime; fibrous as in satiny spar; porous as in calcareous tuffs; specular as in some crystallized plasters; and laminar or cavernous as in some travertines.

Variations from stratified to compact formations can be found in the last series of fractures, and they sometimes include residues of silicified bivalves and quartz veins, which produce serious bonding difficulties since, as the rest of the mass is relatively soft, a crash will certainly break it up, leaving the siliceous parts loose.

Casein adhesives: It would not be fair to speak about rock restoration without considering casein cements. There are few archaeolopetrography collections which do not have any piece preserved with this product; its result has been excellent in most cases, the adhesive has tolerated age in perfect conditions. The caseinates have been considered to be standard elements in cold bondings and it is unlikely to find adhesives used in heavy materials tested for such a long period of time.

These adhesives are based on the combination of casein insoluble in water, and an alkali which neutralizes it and forms the corresponding caseinate. The greater the amount of alkali, the better the casein will disperse, and so, the final product will result more liquid, and the condensing power will consequently decrease. But, when there is a high alkali percentage which depends on the amount of casein, there is no combination, it remains free as a basis. Therefore, a small amount of alkali dissolves a small amount of casein; then, its swelling ap-

titude is maximun profitable. Thus, a neutral adhesive
is achieved, as all the alkali has been combined. Other-
wise, if there is a high percentage of alkali in the ca-
sein will combine, and excessive alkali will result in
the final adhesive, with a very small water - casein re-
lation.

Consolidation of archeological pieces

These operations are frequently mismanaged. Sometimes
the conservators'desperation in salvaging objects in de-
licate conditions, leads them to use materials and methods
which, being exaggeratedly preventive, result in an "over
restoration", which means loosing part of the pieces' va-
lue. Archaeological objects arc the most affected by the-
se "over-restorations" (woods, stones, ceramics, bones,
textiles, metals, etc.) Stone is one of the most over -
restored materials. Macroscopic observation is quite im-
portant in modern geology and essential for preservation.
The conservator does not use the geologist's hammer or,
quite often he does not acceed to sample analysis and is
frequently misled by equivocous appearance of carved sur-
faces; then, crystallography, fails to be an entirely sa-
tisfactory tool for him. Besides, if we consider that,
due to an excessive intervention he is not able to know
the real specific weight, colour, shine, transparency,
smell, flavour, sense of touch, hardness, etc. the scien-
tist becomes a musician playing something by ear.

All this makes the beginner aware of the fact that the
terms "adhesive' and 'consolidant" which normally qualify a
certain product in a list, do not always coincide with
what such words mean for the museum technician. The con-
servator, being a very sensitive and subtle person, can
not ignore the great difference lying between"adhesives"
and"consolidants", will select the properties convenient
for each case and will thoroughly investigate all the po-
ssibilities offered by the dissolutions, dilutions, dis-
persions, mixtures, charges, dosages, etc. When conso-
lidating a rock, we should know, that once it is soaked,
whatever the product may be, it will never recover its
original aspect; we should content ourselves imagining the
way it was. Aware of this, we should operate bearing in
mind both; legitimacy and safety. The intervention should
be carried out through impregnations with aqueous materials
casein emulsions, greasy or synthetic products. There
are few aqueous solution materials used in rock consoli-
dation, as they have been successfully replaced by aque-
ous dispersions, casein ones, and synthetic products.

Cooked fecula pastes with gelatine and flexibilizers
are rarely employed. Methylcellulose is used on painted
rocks, which present flaking in their pictorial layers.
In those cases, the loose flakes are smoothed down with
a resistent tissue paper and methylcellulose solution is
applied pressing it down. Once the paper is dry, it is re-
moved moistening it superficially. The flakes will remain
in place, but then it will be necessary to fix the edges
with P.V.A. and a fine pointed brush.

Casein Emulsions

They are excellent to avoid stains or gloss in the
rocks. They can be prepared putting2,5 g. of casein into
a small glass, adding 15c.c. of water and stirring. Then
two drops of ammonium hydroxide are added, and it is kept
in motion till its final dissolution. This product should
be neutral and, if necessary, it can be lightened with a
little water; and should cracked surfaces occur it can be
suitably mixed with P.V.A.This mixture forms a lumpy pas-
te but it is used pressing on the surface so that it pe-
netrates and fills the cracks.

Greasy Materials

Waxes of different kinds and their combinations, and
other substances are used for consolidation. As the aim
is just to obturate the pores and not to impregnate, so-
metimes it is enough to use cold pastes which harden
through their vehicles evaporation.

The following is an effective product of this kind:

Beeswax	500 g
Carnauba wax	100 g
High melting paraffin	500 g
Colophony	500 g
Dammar	250 g
Mixtox 2 PL 100	5 g

Waxes and paraffin are melted in a double boiler reaching
their top temperature (100°C);the powderized resins are
added and it is stirred until total assimilation.Finally
the Mixtox,previously dissolved in 20c.c. of turpentine
essence, is added,and before cooling down a trichloroe-
thylene and touene (3-2)vehicle is added so as to obtain
a non-flammable liquid.The paste will cool down on the
rock's surface and solvents will evaporate. A thin coat
will remain on the surface, which will be enough to hold
weakened surfaces, especially if the pieces will be shel-
tered. Thus, total imbibitions will be left for rocks in
the open air. Flaking areas can be injected with a conso-
lidant and then holding in place the crust's edges, with
a hard wax applied with a minute hot spatula so that grea-
siness does not flow on the surface damaging the piece.

Synthetic Products

Many synthetic products, dissolved in either solvents
or water, are used in consolidation. P.V.A.in solutions
or dispersions, polymetacrylates with different solvents
and P.V.P. dissolved in alcohol provide excellent conso-
lidations, are amongst the most used. The product, its
fluidity and application, should be carefully selected
or delicate pieces will be hopelessly damaged. Pieces
exposed to periodic imbibitions, and strong erosive winds
can be soaked in: hot wax, caseinates, epoxy resins, poly-
urethanic varnishes, polyester resins, etc. It is useless
to try the same procedure on apparently similar rocks;
rocks do not have a constant composition.

1) The San Bartolo peak is NNW of Cruz del Paramillo in
Uspallata, Mendoza.
2) The Pelado peak is W of Casa de Piedra, Las Heras
Department, Mendoza.

GROTTE DE FONT DE GAUME (LES EYZIES - DORDOGNE - FRANCE) : UN EXEMPLE DE CONSERVATION DES OEUVRES RUPESTRES

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RESUME

Comprendre les mécanismes qui assurent la conservation des cavités nécessite, entre autres, la connaissance des conditions climatiques : circulation de l'air à proximité des parois, température de l'air et de la roche, teneur en vapeur d'eau de l'atmosphère, taux de gaz carbonique. A partir de ce que nous pouvons considérer comme bilan de santé de chaque oeuvre, de chaque cavité, il sera possible de déterminer une intervention pour préserver ou améliorer les conditions de conservation.

1. INTRODUCTION

Depuis la découverte de l'art pariétal et sa reconnaissance officielle, un grand nombre de cavités ont été l'objet de modifications : soit mises en communication avec l'extérieur, soit ont subi des travaux d'aménagement (accès dans les effondrements de l'entrée, percement de tunnel artificiel, installation d'éclairage). La conservation de ce patrimoine archéologique et artistique implique donc des recherches portant, non seulement sur l'oeuvre, mais sur tout son environnement souterrain et aérien extérieur.

Dans une autre communication, nous abordons les problèmes posés par l'environnement géologique et paléokarstique d'une cavité, intervenant dans le maintien des facteurs assurant des conditions optimales de conservation ; il convenait après de se tourner vers le milieu interne, le cas échéant.

A partir de ce que nous pouvons considérer comme un bilan de santé de chaque grotte ornée, il sera possible de décider une intervention pour prévenir et améliorer les conditions de conservation, chaque cavité étant un cas particulier aux comportements spécifiques. Nous illustrerons notre propos à l'aide de l'exemple de la grotte de Font de Gaume aux Eyzies en Dordogne (France) où, par sa localisation en pleine région touristique -région où la connaissance des activités humaines préhistoriques est un vecteur principal de l'animation culturelle-, la cavité pouvait être l'objet de dégradations irrémédiables dues à une fréquentation trop intense.

2. RAPPELS MORPHOLOGIQUES ET HYDROGEOLOGIQUES

La grotte de Font de Gaume mesure 124 m de long et a de 2 à 8 m de haut ; elle est creusée aux deux tiers de la falaise et l'entrée est à environ une vingtaine de mètres au-dessus de la cote du fond du vallon (cf. plan fig. n° 1). Elle comporte une galerie principale sur laquelle viennent s'adjoindre un premier diverticule coudé accédant directement à l'extérieur, une petite galerie, et dans la partie décorée après l'étroiture dite du "Rubicon", un diverticule latéral et une petite salle "le Cabinet des Bisons". Sur le plan hydrogéologique, c'est un réseau de niveau moyen qui fait partie de la fraction supérieure de l'étage Coniacien qui est un puissant horizon calcaréo-gréseux.

Les études du Centre d'Hydrogéologie de l'Université de Bordeaux I ont montré que le conduit principal s'est mis en place de part et d'autre d'un plan de diaclase subverticale et les conduits annexes se sont développés le long de diaclases perpenduculaires à la galerie

principale. La genèse de la cavité a donc été très marquée par les accidents structuraux du plateau.

Les observations faites à l'intérieur de la grotte, en relation avec l'étude pluviométrique régionale, nous amènent à constater que :

. la grotte ornée n'est pas affectée par des venues d'eau importantes en débit,
. les venues sont à la fois ponctuelles (au droit d'un concrétionnement) et étalées (sur des surfaces rocheuses poreuses perméables en petit),
. la liaison hydrogéologique verticale ou subverticale entre la surface et la cavité, se fait pour partie le long de rares diaclases verticales et pour partie par l'intermédiaire de bancs à perméabilité de canalicules et de pores,
. la mise en réserve est importante,
. le retard à l'écoulement, comparé à d'autres réseaux karstiques, est élevé et voisin de 5 mois pour la partie ornée de la grotte et plus important pour les parties profondes du réseau. Cette "réaction hydrogéologique" est associée au rythme des pluies, de l'évapotranspiration (associée aux plantes) et à la géométrie des calcaires au-dessus de la cavité.

3. CARACTERISTIQUES DU MILIEU INTERNE

Les études faites dans les cavités ont montré que toute grotte possède son climat propre qui est plus ou moins directement lié aux variations climatiques externes ; les températures, l'humidité de l'air et des parois dépendent de la propagation des ondes thermiques à travers les terrains surincombants, des précipitations extérieures, et des échanges gazeux entre l'intérieur et l'extérieur. Pour Font de Gaume comme pour les autres cavités aménagées, s'ajoute la perturbation due aux visiteurs. L'hygrométrie, la température, le taux de gaz carbonique, la ventilation des galeries, déterminent pour chaque caverne suivant sa morphologie, un régime climatique particulier ; il n'est pas stable, et il évolue tout au long de l'année et dans le temps ; un cycle régulier tend donc à s'instaurer.

Les travaux de M. Breuil servent encore de référence et permettent de distinguer 80 bisons, 40 chevaux, 23 mammouths, 17 cervidés et rennes, 8 bodidés, 4 capridés, 2 rhinocéros, 1 ou 2 félins, 1 loup, 1 ours, 1 représentation humaine, 4 mains négatives, 19 tectiformes, 5 ou 6 signes variés.

Les peintures et gravures rupestres des cavités ont pu être préservées pendant plusieurs milliers d'années grâce à des conditions d'exceptionnelle stabilité du microclimat dû à la combinaison heureuse des différents paramètres ; cet équilibre est fragile (cf. photos n° 1 et 2).
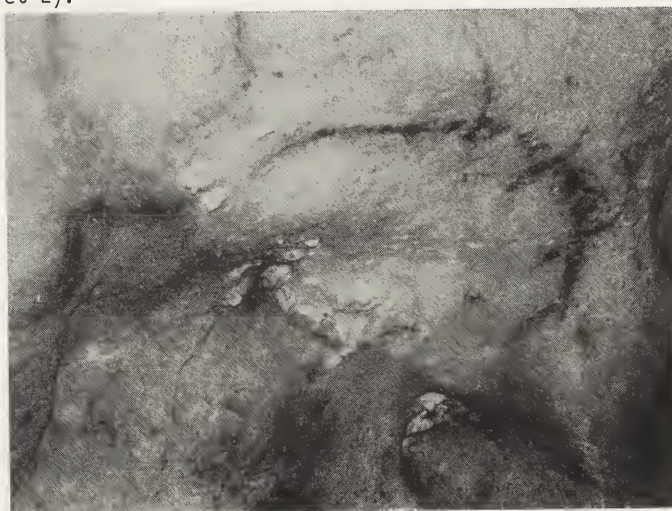
Photo n° 1 : Bison. Cliché L.R.M.H.

Il était donc important de connaître les différentes caractéristiques de Font de Gaume, d'observer les variations naturelles de ces paramètres et celles consécutives aux visiteurs pour mieux définir un rythme de fréquentation en harmonie avec la conservation des peintures et des gravures.

GROTTE DE FONT DE GAUME (LES EYZIES - DORDOGNE - FRANCE) : UN EXEMPLE DE CONSERVATION DES OEUVRES RUPESTRES
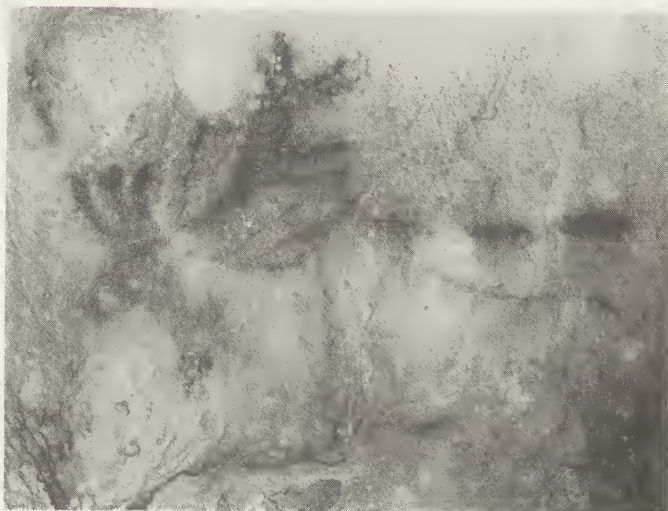
Photo n° 2 : Renne à imposante ramure en superposition avec un tracé de cheval ; un voile de calcite recouvre inégalement la roche. Cliché L.R.M.H.

3.1. Etude thermique

Les températures de l'air et de la roche sont des paramètres importants du régime général de la grotte ; elles ont été relevées à l'aide de thermomètres (+5/+20°C) au 1/20è de degré d'appréciation, placés à demeure dans l'air et la roche. Les courbes les plus représentatives de ces mesures de décembre 1972 à novembre 1973 (cf. fig.2) montrent :

. deux régimes distincts de part et d'autre de l'étroiture du "Rubicon",
. la fourchette (12 à 13°) des températures de la première partie,
. celle (13 à 14°) de la deuxième partie, durant les trois quarts de l'année,
. l'influence des visites de juillet à septembre 1973, où les températures de la première partie rejoignent la fourchette supérieure, tandis que celles de la deuxième partie augmentent aussi corrélativement en dépit de la fréquentation touristique déjà limitée (600 personnes par jour à l'époque).

Des multiples mesures réalisées de 1965 à 1983 pendant et en-dehors de la fréquentation touristique, sans ou avec limitation de visite, il ressort que la grotte peut être scindée en deux parties. La première comprend les deux entrées et la galerie d'accès jusqu'à l'étroiture du "Rubicon", la seconde comprend tout le reste de la cavité. Cette situation naturelle est la raison majeure de la conservation des oeuvres d'art dans la 3e partie(1).

3.2. Dynamique de l'air

A proximité des parois, la vitesse et la direction des masses d'air oriente les échanges gazeux et il est important d'appréhender dans le volume d'une cavité la distribution des courants d'air.

Au lieu d'utiliser de petits ballons de caoutchouc gonflés à l'hélium, nous avons préféré la méthode mise au point à Lascaux sous la forme de petits flotteurs en polystyrène expansé doté d'un volume uniforme et flottant à la surface d'un plan d'eau fourni par un bac.

Sous l'effet du courant d'air, le flotteur se déplace d'un bord à l'autre et le volume régulier de la portion de flotteur fournit la direction du courant d'air. Plusieurs dizaines de bacs ainsi équipés permettent ainsi de suivre l'évolution des masses d'air d'une galerie.

(1) Un examen méticuleux récent des parois de cette première partie par des préhistoriens (A. Roussot et N. Aujoulat) a permis la mise en évidence de tracés dans les portions de parois très concrétionnées mais en moins bon état.

Nous rappellerons que deux régimes de circulation de l'air ont été reconnus globalement à Font de Gaume. En hiver, l'air extérieur exerce son influence en créant un courant d'air plus froid à partir du diverticule coudé communiquant avec l'extérieur au niveau du sol ; tout le long des galeries, l'air de la cavité plus chaud est refoulé et circule en partie haute. L'été, ce schéma s'inverse, l'air extérieur, chaud, pénètre en partie haute et chasse l'air interne, plus frais, au niveau du sol.

Ces deux schémas sont valables pour le cas où la porte d'entrée est fermée ; ils correspondent à l'état actuel du réseau ; la galerie d'accès joue dans ce cas le rôle de cul-de-sac pour la circulation d'air décrite, et la porte peut faire office d'échangeur thermique. Ces deux régimes sont soumis à de nombreuses variations suivant l'ensoleillement des entrées, les fluctuations thermiques jour-nuit, la pression atmosphérique et la fréquentation de la cavité.

Font de Gaume est une cavité du type "piège à air chaud" et l'air chaud pénètre difficilement dans la partie ornée qui subsiste grâce à la présence de l'obstacle créé par ce rétrécissement. En hiver, pour des raisons identiques, l'air froid a des difficultés à cheminer jusqu'au fond. De tout ceci, il résulte une relative constance des températures.

3.3. Etude du taux de gaz carbonique

Les mesures systématiques faites matin et soir, soit avant et après les visites, au cours des années 1969 et 1971 à une période où il n'y avait pas de limitation de visite, en divers points du réseau ont permis d'apprécier les conséquences directes du séjour des visites et ont révélé :

. l'existence d'un taux de gaz carbonique de l'ordre de 0,1 à 0,3 % d'une manière naturelle ; cette faible teneur correspond aux valeurs notées par ailleurs dans ce type de cavité subhorizontale. Ce gaz est d'origine pédologique, il est dû aux mécanismes de dégradation de la matière organique dans les horizons superficiels du sol,
. un cycle annuel de la variation du gaz carbonique,
. une étroite relation entre la teneur de gaz et le nombre des visiteurs,
. le rôle de l'étroiture du "Rubicon" ; dans la partie décorée, nous avons noté 2 % de CO_2 lorsque le nombre de visiteurs est supérieur à 800, la teneur ne descend pas au-dessous de 1 % durant les 3 mois de visites estivales à l'époque,
. la possibilité sur un cycle journalier d'une élimination naturelle grâce à la circulation normale de l'air en dépit de cet obstacle.

4. RECOMMANDATIONS ET MESURES PRISES

Après plusieurs cycles annuels d'études visant à suivre l'évolution des températures, de l'humidité et du gaz carbonique, nous avons été conduits à conseiller une limitation de la fréquentation de la cavité, pour mieux maitriser et contrôler l'évolution calcique des parois qui dépend entre autre de la pression partielle de CO_2 (rappel), ce dernier étant produit par les visiteurs.

La cavité est dans un environnement soumis aux variations externes et, à certaines périodes de l'année (hiver, printemps), quelques parties des parois ornées et concrétionnées sont exposées aux ruissellements des eaux d'infiltration ; à d'autres périodes (été), à part les pluies d'orage dont l'influence est limitée par l'évapotranspiration, seul le phénomène de condensation constitue une menace par le risque de dissolution.

Dans ces conditions, l'idéal serait en théorie, d'une part de ne pas trop abaisser le taux de CO_2 présent dans la grotte lorsqu'il y a ruissellement afin de diminuer au maximum la précipitation de carbonate sur les parois et d'autre part d'éliminer ce gaz lorsqu'il n'y a plus sur les parois que l'eau de condensation provenant de l'air. C'est la solution vers laquelle nous nous sommes efforcés de tendre, l'été en éliminant le gaz carbonique et en restreignant la fréquentation touristique et, l'hiver en laissant la cavité retrouver un régime proche des conditions normales qui ont dû régner pendant des millénaires et avant la découverte des peintures.
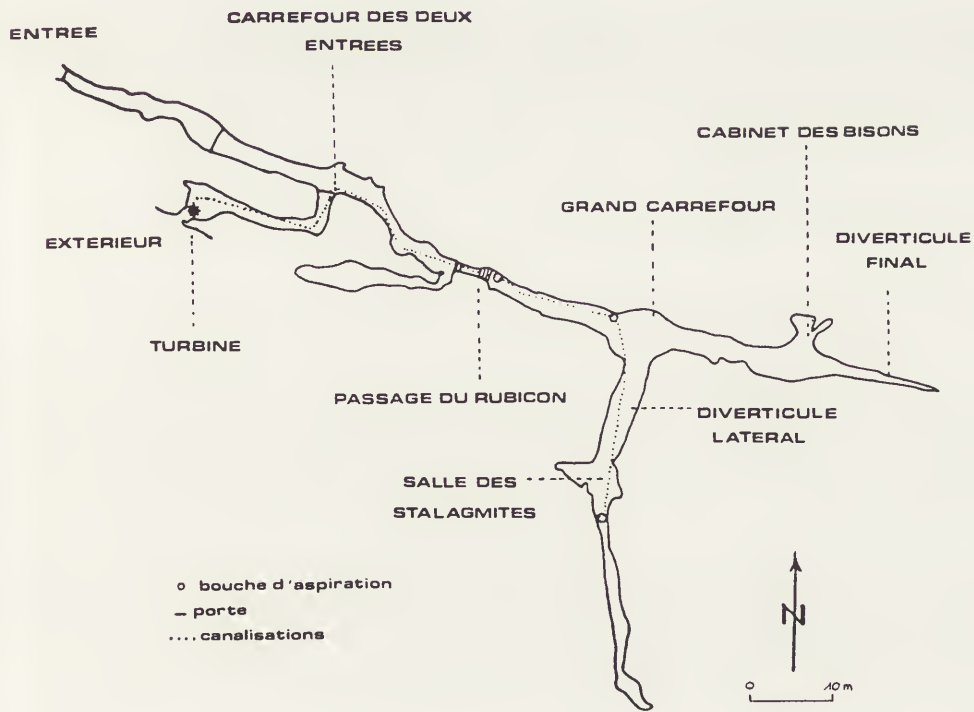
Fig.1 : Plan de la grotte de Font de Gaume aux Eyzies,
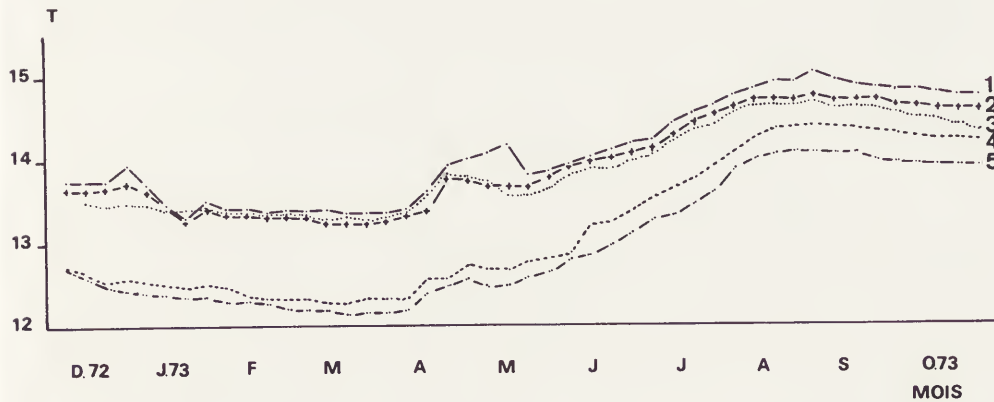Dordogne (France).

Fig.2 : Courbes représentatives de la variation de
température, de décembre 1972 à octobre 1973 :

- courbe 1 : température de l'air au grand carrefour
- courbe 2 : température de la roche au grand carrefour
- courbe 3 : température de l'air à l'interface air-
             roche au cabinet des bisons
- courbe 4 : température de l'air à l'interface air-
             roche au carrefour des deux entrées
- courbe 5 : température de la roche au carrefour des
             2 entrées.

L'élimination du gaz carbonique a été favorisée par
l'établissement d'une légère dépression qui améliore
les échanges d'air entre la section décorée et la par-
tie d'accès avec les deux entrées . Le déficit d'air
est compensé d'une manière diffuse et se renouvelle
progressivement par la première partie et à travers les
fissures de la roche.

De nombreux contrôles ont été réalisés après la mise
en place du dispositif d'élimination (3 bouches d'as-
piration au niveau du sol) ; nous donnerons, à titre
d'exemple, celui de juillet 1977 où des mesures ont été
faites heure par heure pendant la visite pour une jour-
née où 550 personnes sont entrées dans la cavité, ré-
parties le matin et l'après-midi.

Le lendemain après le fonctionnement de la turbine tou-
te la nuit, le taux de gaz carbonique est inférieur à
0,1 %, l'accumulation d'un jour à l'autre n'existe
plus.

5. CONCLUSION

Les études et interventions décrites ont permis de mai-
triser l'influence du gaz carbonique et de rendre en
période touristique à la grotte de Font de Gaume des
conditions favorables à la conservation des figures ru-
pestres.

Dans cette cavité de faible volume, l'incidence de tou-
te perturbation est immédiate ; néanmoins nous pouvons
actuellement maintenir un équilibre qui reste précaire
et qu'il convient de ne pas modifier en changeant les
conditions de base de l'étude.

Font de Gaume est sous surveillance scientifique et,
régulièrement, des contrôles pour détecter d'éventuel-
les modifications ont lieu ; c'est grâce à ce travail
régulier qu'il est possible d'assurer la protection et
la conservation de ce patrimoine artistique.

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A PROPOS DE LA PROTECTION DE L'ENVIRONNEMENT DES MONU-
MENTS RUPESTRES ORNES DU PATRIMOINE MONDIAL - MYTHE OU
REALITE ?

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RESUME

A l'heure où l'on découvre de nouveaux monuments ornés,
tant en grottes (Dordogne-France) que sous abris
(Sahara) il est encore temps d'aborder dans son ensem-
ble et à l'échelle mondiale le double problème de la
conservation des oeuvres rupestres et de la protection
des sites qui leur sont associés. Ce bref exposé n'a
pas la prétention de résoudre tous les captivants mys-
tères qui entourent encore cette discipline. Il s'agit
dans un premier temps de décrire une méthodologie d'ap-
proche rodée de longue date et de présenter par l'image
quelques résultats importants acquis au cours d'une
vingtaine d'années de recherches fondamentales et appli-
quées sur le sujet.

1. GENERALITES

Il existe des monuments rupestres pour lesquels la dé-
térioration est naturelle et liée :
à l'eau - aux courants d'air - au soleil - au gaz car-
bonique - à la microfaune - à la microflore etc...

Pour ne prendre qu'un exemple, sur une surface rocheu-
se peinte de 3550 m² au total, il faut savoir que dans
la grotte de Lascaux, il y a 330 m² environ (soit 9,3%)
qui ont été, autrefois, totalement détruits par une
ventilation forcée qui traversait deux étages altimé-
triquement et thermiquement différents au sein du ré-
seau karstique.

Des détériorations artificielles, c'est-à-dire héritées
de la fréquentation et/ou de l'activité humaine s'ajou-
tent à la liste précédente. Ces détériorations affec-
tent aussi bien l'environnement aérien, sub-aérien que
souterrain.

Nous citons ci-dessous quelques exemples caractéristi-
ques que nous avons extraits d'une longue liste de
causes très diverses.

a) pour l'environnement naturel aérien et souterrain :
la pratique moderne de la culture - de l'élevage - de
la gestion des bois et forêts - de l'urbanisme - de
l'industrie et..... du tourisme !

b) pour l'action directe sur les parois :
les frottis - les graffitis - l'échauffement artificiel
pour le tournage de films etc...

Parmi tous ces altéragènes, l'eau est ou a été un vec-
teur privilégié qui assure (ou qui assurait) indistinc-
tement le transfert de frigories - de calories - de
substances minérales et organiques dissoutes ainsi qu'
un cortège associé à la microflore et à la microfaune.

La migration du flux hydrique se fait à travers les fis-
sures, les joints et les diaclases élargies qui compar-
timentent les terrains carbonatés (de la craie aux cal-
caires marneux et sans oublier les grès).

La concentration des éléments qui sont entraînés per
descensum peut être "anormale" ou "normale", c'est-à-
dire qu'elle peut dépasser ou non un seuil qui a été
fixé par l'expérience ou a priori.

Dans le cas d'une concentration "anormale", les risques
de détériorations et de pollutions sont susceptibles
de se manifester à proximité et sur des peintures et
des gravures.

Quelques actions, parmi les plus fréquentes, sont citées
ci-dessous dans le domaine minéral (a) et organique
(b) :

(a)-concrétionnement - dissolution - désagrégation
mécanique - écaillage - empoussiérage - mutation chro-
matique,
(b)-essaimage - mutation chromatique - dépigmentation -
épidémiologie algale et bactérienne.

2. LE ROLE DU MILIEU GEOLOGIQUE

Le transfert des éléments polluants et destructifs
(altéragènes), dépend essentiellement des conditions
climatiques et de la nature du cadre géologique au
sein duquel sont creusés les abris sous roches, les
falaises, les grottes-abris et les grottes.

Présentement, nous évoquerons uniquement les strates
carbonatées et les réseaux creusés dans les bassins
sédimentaires.

Les transferts de flux et d'éléments dissous ou de très
petite taille vont s'effectuer à travers un toit, une
voûte, un porche, un auvent plus ou moins épais, poreux,
perméable et fissuré.

La nature lithologique et l'architecture interne de ces
terrains vont guider le flux hydrique, jouer sur la vi-
tesse de transfert du fluide et le piégeage plus ou
moins grand des éléments associés à l'eau.

A propos de cette architecture souterraine, il existe
des schémas naturels favorables à la limitation des
risques de pollution.

La compacité des roches et la rareté des fissures sont
des éléments favorables. Ce cas idéal correspond au
schéma (A) - cf. ci-après. Il se rencontre très rare-
ment. Ici, la voûte marneuse semi-perméable ralentit
le flux hydrique et facilite les échanges ioniques et
le piégeage au-dessus du réseau orné, creusé dans les
calcaires.

Le cas le plus fréquent correspond au schéma (B) asso-
cié à une couche unique et épaisse de calcaire (cf.
page suivante).

Ici, les transferts verticaux et sub-verticaux sont
plus ou moins rapides ou lents selon la taille, l'ex-
tension, l'interconnexion et le degré de comblement du
réseau de fente dont la trame inférieure reste proche
ou atteint la ou les surfaces peintes et gravées.

3. PROTECTION DES SITES ET PREVENTIONS DES NUISANCES

Les perturbations potentielles susceptibles de détério-
rer les oeuvres d'art rupestres viennent, pour une part,
de la surface topographique et des activités qui lui
sont associées.

Dans des régions à vocation agricole évolutive et tou-
ristique affirmée, par exemple, l'impact des traite-
ments chimiques d'une part, la pression de la construc-
tibilité d'autre part (sous la forme de résidences se-
condaires, motels, caravaning etc...) s'accentuent dans
des zones où la planification de l'occupation du sol
(P.O.S.) n'est pas toujours réalisée ni même quelque-
fois envisagée.

L'eau d'infiltration y joue un rôle de relais qui peut
être des plus défavorables.

Pour chaque site étudié, il existe une topographie
aérienne de géométrie plus ou moins complexe à partir
de laquelle l'eau qui ruisselle ou qui s'infiltre peut
atteindre, après un parcours plus ou moins long, une
surface peinte et/ou gravée.

Il s'agit de l'impluvium, lequel peut constituer selon
l'histoire géologique et climatique un système monocou-
che (terrain nu) ou bicouche (sol+terrain) avec couver-
ture herbeuse ou arborescente (cf. schéma -C-).

Dans un tel contexte la prévision des risques de nui-
sances est possible à partir de la mesure des capacités
d'infiltration de l'interface air-sol ou air-roche. Elle
doit être répétée en chaque lieu qui est chaque fois un
cas d'espèce.

Le but final étendu à un grand nombre de sites sous dif-
férents climats est bien entendu d'établir une typologie
et progressivement une cartographie des risques de nui-
sances adaptée aux activités les plus fréquentes.
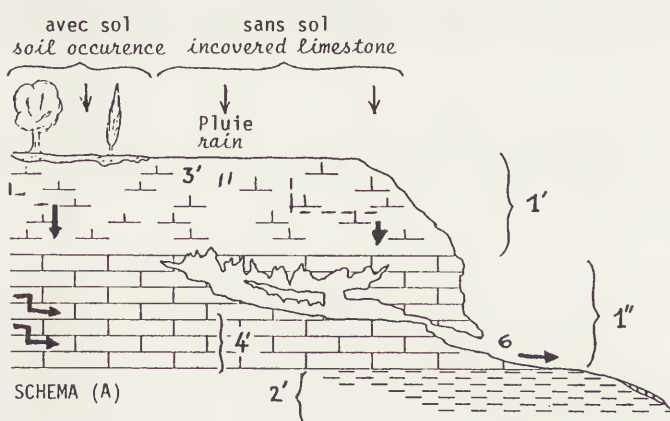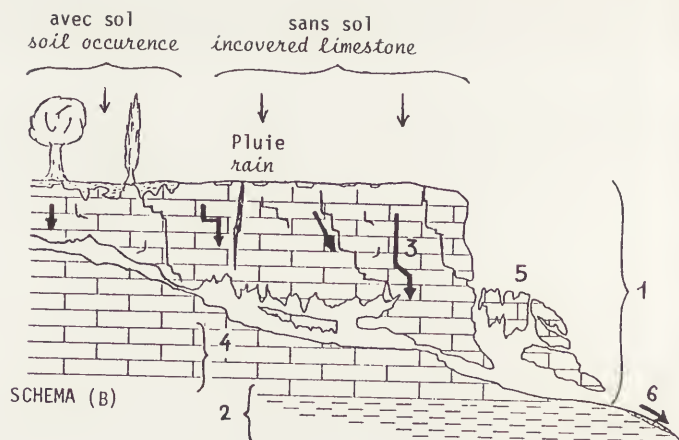
SCHEMA (A)

SCHEMA (B)

Schéma (A) - (1') horizon microfissuré et non karsti-
fiable (marnes) - (1") horizon karstifiable avec réseau
unique - (2') niveau imperméable - (3') microcircula-
tions d'eau et percolations - (4') terrains saturés et
alimentation par l'arrière - (6) source.

Sketch (A) - (1') microkarstic geological horizon
covered by marl - (1") single and dipping net -
(2') impervious layer - (3') micro water circulation
and percolation - (4') saturated formations and back
supply - (6) spring.

LEGENDE

Schéma (B) - (1) horizon karstifiable avec réseau à
étages - (2) niveau imperméable - (3) infiltration par
réseau de fissures et chenaux dans terrains non satu-
rés - (4) terrains saturés - nappe discontinue -
(5) formes karstiques (aven-puits etc...) - (6) source.

LEGEND

Sketch (B) - (1) karstic geological horizon with level
net - (2) impervious level - (3) infiltration in cra-
king zone of aeration - (4) saturated formations - dis-
continuity waterbearing - (5) karstic and landforms -
(6) spring.
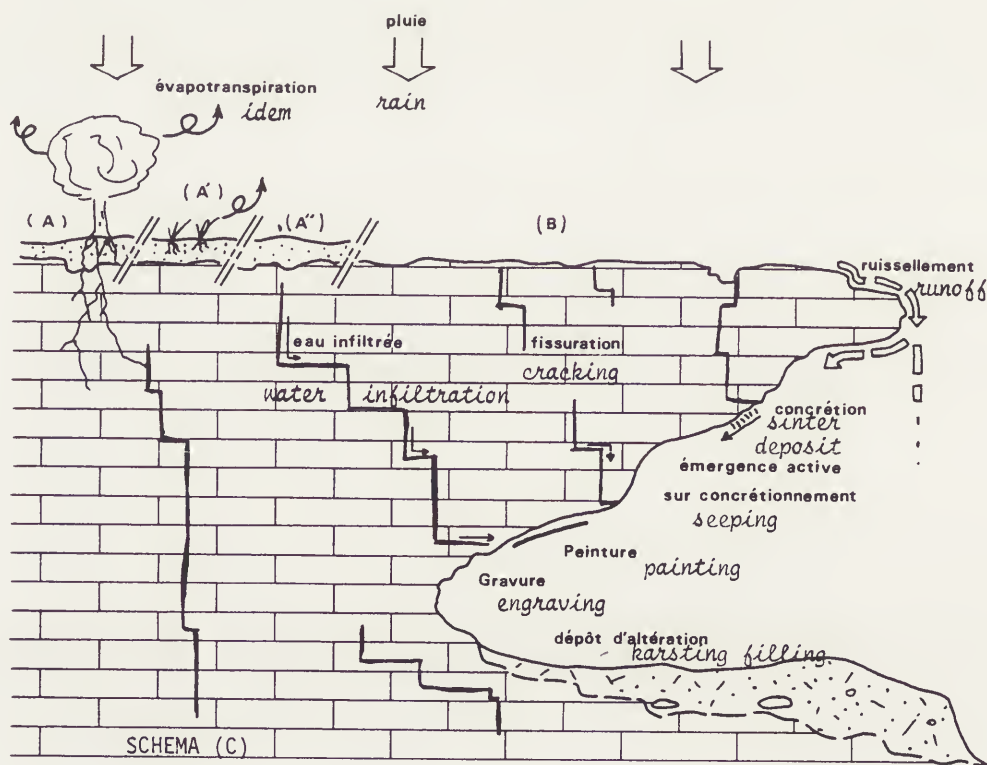
SCHEMA (C)

Schéma synthétique d'une grotte-abri creusée en milieu
calcaréo-gréseux fissuré et cadre hydrogéologique.
(A) - sol sur calcaire, avec végétation arbustive.
(A')- sol sur calcaire avec couverture harbacée.
(A")- sol nu.
(B) - calcaire dénudé et altéré.

Synthetic sketch of a shelter cave excavated in craked
limestone, with hydrogeological set.
(A) - soil on limestone with trees.
(A')- soil on limestone with grass or dry moor.
(A")- incovered soil.
(B) - incovered weathered limestone.

L'inventaire du cadre naturel, des activités humaines,
de l'habitat, associé à la mesure de certains paramè-
tres in-situ, permettent ainsi d'établir une carte de
vulnérabilité de l'impluvium.

Elle précise les limites géographiques, en-deça des-
quelles le site rupestre est ou sera affecté par tel
ou tel phénomène. Nous avons établi à la suite une
échelle des risques. Cela se traduit au sol par un
sous-zonage pour lequel la valeur de l'indice choisi
est inversement proportionnel au risque encouru.

Ainsi la zone n° 1 est celle où le cheminement souter-
rain des eaux sera le plus bref et où la vulnérabilité
sera la plus grande (cf. schéma -D-), etc...).

4. BILAN

Les études pluridisciplinaires que nous menons depuis
de nombreuses années tant en France qu'à l'étranger,
révèlent chaque fois l'importance des échanges entre
l'atmosphère et le sous-sol.

Dans la tranche d'hétérothermie, l'effet climatique
(calories, frigories, eaux d'infiltration) se fait sen-
tir avec une intensité et un retard plus ou moins
grands selon la latitude, l'altitude, la présence ou
l'absence de végétation, la nature et l'architecture
du substratum géologique.

L'eau, pour sa part, peut modifier la nature et les
qualités de la surface d'échange que constituent les
parois et voûtes des cavités par l'intermédiaire du
concrétionnement.

Ces paramètres influent individuellement et/ou globale-
ment sur l'équilibre climatique interne des grottes et
grottes-abris.

La climatologie interne, c'est-à-dire associée à l'air
des réseaux souterrains fait l'objet d'un développe-
ment particulier rédigé par P. Vidal et J. Vouvé à la
suite du présent article. Une autre note présentée par
J. Brunet et P. Vidal évoquera, en prolongement des
deux premières, un aspect de l'évolution minéralogique
et picturale sur les parois.

Pour revenir à la protection des sites, celle-ci n'a
d'intérêt que si elle peut reposer sur une base juri-
dique officielle puisqu'elle intègre la propriété pri-
vée entre autre pour laquelle des contraintes seront
imposées règlementairement (cf. tableau ci-après).

Elle représente un atout capital dans la mesure où elle
précède la conservation au sens large puisque la pré-
vention et l'action au niveau des peintures, des gravu-
res et des enceintes souterraines sont techniquement
réalisables sous diverses formes :
fixage - collage - ablation ponctuelle et élargie du
concrétionnement, des voiles etc... - extraction des
gaz - climatisation.

5. CONCLUSIONS

La présentation que nous venons de faire, n'a d'autre
prétention que d'inciter les responsables scientifi-
ques et administratifs à une sorte d'examen de cons-
cience à propos du problème de la conservation des
grottes ornées. Cette action doit obligatoirement être
précédée par la protection de l'environnement naturel
qui lui est associé et dont les dimensions et l'acti-
vité (naturelle, économique etc...) sont chaque fois
différentes.

L'eau et son cheminement aérien et souterrain, sont
deux guides précieux dont l'identification permettra
de cerner et de quantifier la vulnérabilité du monu-
ment orné à l'égard des nuisances (s.l.).

Cette démarche s'applique sous les climats de type
tempéré, méditerranéen, continental et assimilés. Elle
reste digne d'intérêt en climat sub-désertique et dé-
sertique. Dans ce dernier cas, l'analyse paléoclimati-
que et paléohydrogéologique doit précéder l'approche
scientifique classique.

Nous retiendrons en définitive que la protection de
l'environnement et la conservation des oeuvres rupes-
tres sont devenues deux réalités pratiques. C.Q.F.D.
(en toutes lettres = ce qu'il fallait démontrer).

Dans le monde, ce qui n'est encore qu'actions ponc-
tuelles et isolées doit être élargi sur la base de pro-
grammes coordonnés à moyen et à long terme. Pour la
France, le L.R.M.H. et le C.H. associés dans les études
de terrain, jouent ce rôle et nous ne pouvons que nous
en féliciter.

LA GRENOUILLE
LES GIROUTEAUX
falaise "cliff"
D. 47
ZONE 3
ZONE 2
186
Grte DE FONT DE GAUME
ZONE 1
Les Eyzies-de-Tayac
ZONE 3
188
BEUNE
limite de l'impluvium "limit of impluvium"
D. 48
0   200m

CARTE DE VULNERABILITE
SCHEMA (D)
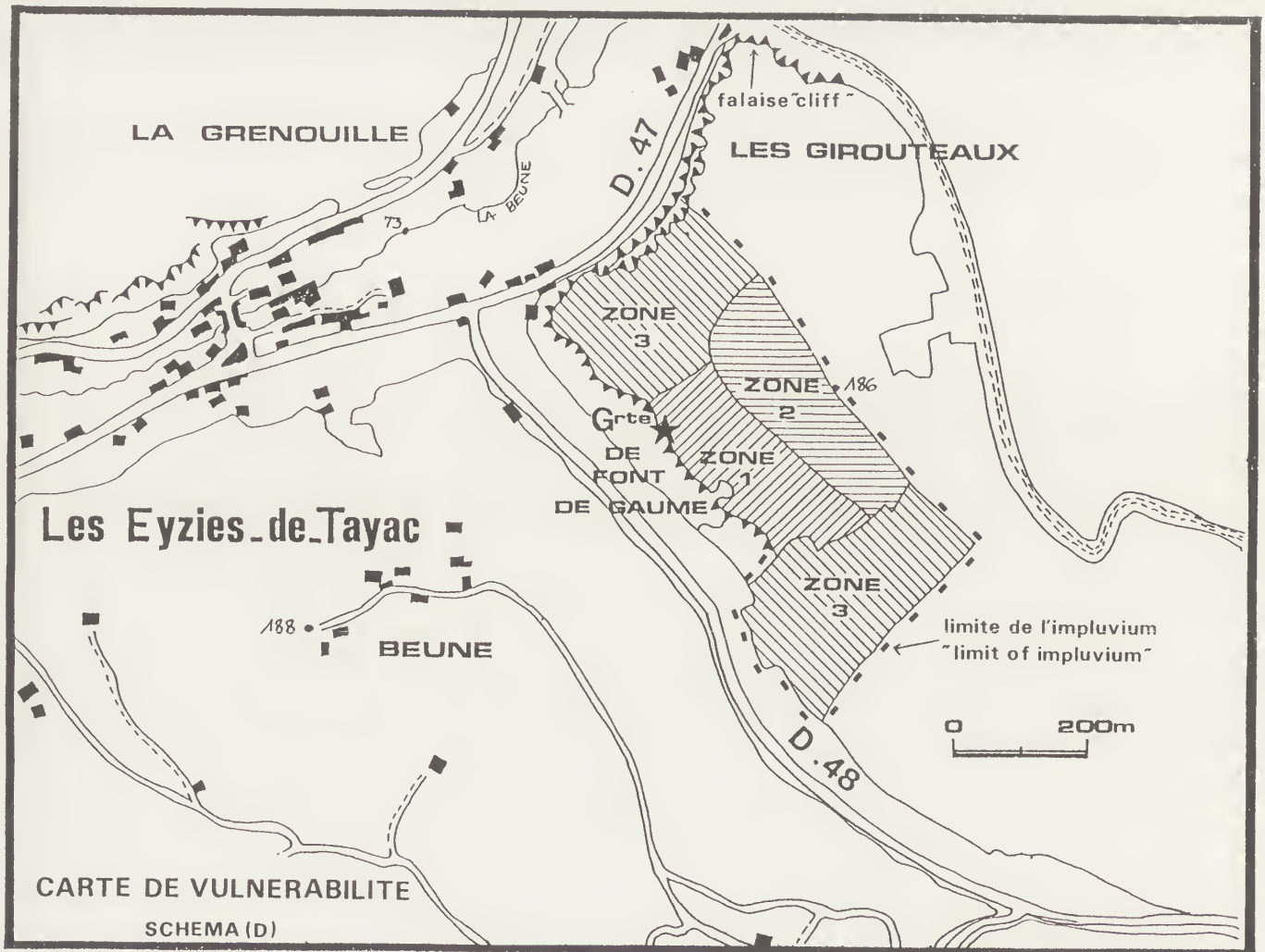
LEGENDE - L'inventaire des risques de nuisances asso-
cié à l'impluvium qui domine la grotte de Font de Gaume
a permis de dessiner une carte de vulnérabilité décou-
pée en 3 zones (cf. tableau détaillé).

LEGEND - The present sketch is a map of vulnerability
on the impluvium from Font de Gaume' cave. Zone 1, is
the most vulnerable class. Zone 2, is the middle class.
Zone 3, is the small class.

SITE DE FONT DE GAUME

N° zone		Nature surface	Appartenance hydrogéologique	Pollution potentielle estimée	Activités interdites	Activités règlementées
I M P L U V I U M	1	pente sol forte sol mince caillouteux et sol absent rocher affleurant calcaire fissuré couverture végétale : - chênes uniquement + lande	dépendance directe temps de transfert : entre 3 et 4 mois	forte	- déboisement - aménagements divers - constructibilité - culture - activités indus-trielles et tou-ristiques	-
	2	pente sol moyenne sol caillouteux, mince + sol argileux moyen calcaire affleurant moyennement fissuré calcaire subaffleurant couverture végétale : chênes 90 % et pins sylvestres 10 %	dépendance directe et moyenne temps de transfert : entre 4 et 6 mois	forte à moyenne	- aménagements divers - constructibilité - activités indus-trielles - amandements (engrais naturels et chimiques)	- déboisement sur petites surfaces avec obligation -reboisement
	3	pente sol moyenne sol argilo-calcaire et sol nu calcaire subaffleurant et affleurant peu fissuré couverture végétale : chênes	dépendance retar-dée temps de transfert : entre 8 et 10 mois	moyenne à faible	- activités indus-trielles et tou-ristiques	- constructibilité - aménagements divers

Section 25

Bio-deterioration of Museum
Collections

Bio-détérioration des collections
du musée

STUDIES ON FUNGAL RESISTANCE OF BIRCH-BARK

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SUMMARY

The effect of humidity and temperature on
the growth of test fungus (a. niger) on
birch-bark was studied by placing equal
sized birch-bark and Whatman filter papers
impregnated with nutritive media, at
different humidity and temperatures. The
paper pieces were used as reference points.
Birch-bark was found to be very fungus
resistant even at high humidity. Tests
were also conducted on birch-bark leached
with different organic solvents. Not much
difference is seen between the behaviour
of the treated and untreated samples.

INTRODUCTION

It is well-known that the climatic condi-
tions inside the storage and the exhibition
areas in a museum have a profound effect
on the preservation of objects. In the
Tropical countries, where the relative
humidity is quite high for the major part
of the year, there is always a danger of
fungal growth on hygroscopic and nutritive
materials, like paper and textiles. For
this reason, fungal attack is a major
factor to be taken into consideration for
the conservation of materials in the
Tropics.

In India, before the advent of paper,
birch-bark along with the palm-leaf was a
common writing material. Large collect-
ions of birch-bark manuscripts exist today
in several Indian museums. It is commonly
observed that birch-bark keeps supple and
flexible in slightly humid atmosphere and
tends to become brittle in dry conditions.
It was, therefore, felt necessary that
certain standards be formulated for the
storage of birch-bark manuscripts. In the
first phase of our study, the inter-
relationship of the climatic conditions
on the growth of fungi or birch-bark was
taken up.

Normally, birch-bark manuscripts are not
affected by fungi and insects. In many a
case in which the birch-bark page had been
repaired with paper, paper strips were
damaged by fungi or insects leaving the
birch-bark itself unharmed. This observa-
tion indicated that the birch-bark
contained some ingredient which was acting
as a repellent to fungi and insects.
However, recently while examining some
manuscripts on birch-bark, fungus was
noticed on some of them. But even this
growth was practically superficial and had
not penetrated deep into the material.

In order to understand the phenomenon
further, some studies were initiated at
our Laboratory, with the intention to :

(i)   to find out the role of humidity
        and temperature on fungal growth
        on birch-bark.

(ii)   to ascertain the extent of fungal
        growth on birch-bark leached with
        organic solvents. This study was
        necessary because organic solvents
        are often used for cleaning
        manuscripts.

(iii)   to ascertain whether birch-bark can
        be used as an anti-fungal agent for
        other objects, like paper manuscri-
        pts. The purpose of this experiment
        was to know if the anti-fungal
        property of birch-bark could be
        utilised for the safety of other
        materials by placing birch-bark
        alongwith them in storage.

ROLE OF TEMPERATURE AND RELATIVE HUMIDITY ON FUNGAL GROWTH

For this experiment, pieces of equal size
of birch-bark and Whatman filter paper
as reference were used for comparative
study of growth of fungi under varying
conditions of temperature and relative
humidity. The pieces of filter paper
were impregnated with Eggins and Pugh
nutrients, autoclaved and dried in an
oven at 80°C for three days.[1] The birch-
bark pieces were cleaned with sterile
water and dried under laminar flow. Both
the dried birch-bark and paper pieces were
dusted with the spores of A. niger
(a test fungus) and hung inside glass jars
with the help of plastic clamps.

Several such sets were prepared. For
maintaining different humidity conditions,
various saturated solutions were used and
for varying temperatures the jars were
placed inside the incubators maintained
at 20, 25, 30 and 35°C. Control sets
were run without any fungal spray. All
the sets were checked after each four
days, to see if there was any growth of
fungus. Categorization was done by
visual observation (Tables 1 to 4).

RESULTS

It is evident from the results mentioned
in Table 1 that there is no fungal growth
on birch-bark to a very great extent. No
fungal growth was observed upto 28 days
when the temperature was 20°C and relative
humidity was raised as high as 100%
starting from 52%. In the case of paper,
the growth was observed after 12 days
at 100% R.H., after 20 days at 85% R.H.
and after 24 days at 75% and none at
52 or 64%.

When the temperature was maintained at
25°C, no growth was observed under relative
humidity conditions from 52 to 84%. A
very thin growth was observed only on the
28th day at 100% R.H. On the other hand,
in the case of paper, a thin fungal growth
was observed on the 8th day at 100% R.H.
This growth gradually increased and the
paper was badly rotted on the 28th day.

At 85% and 75% R.H. fungus was observed after 16 and 20 days respectively. No fungal growth was observed at 52 or 64% R.H.

Table 3 gives the results of the fungal growth at different relative humidities and 30°C temperature. At this temperature and 100% and 85% R.H., a thin fungal growth was observed after 20 and 28 days on birch-bark. While on paper it started appearing only after 4 days, 12 days and 20 days at 100%, 85% and 75% R.H. At 100% R.H., the paper piece was completely covered with fungus on the 16th day.

Table 4 shows the results of the fungal growth at 35°C in differing R.H. conditions. On birch-bark, the results were similar to those in the case of 30°C temperature. On paper, the growth started on the fourth day at 100% R.H., completely covering it on the 12th day. At 85% and 75% R.H. the growth on paper was observed on the 8th and 16th day. No fungal growth was observed at 64% and 52% R.H.

It can be concluded from the above observations that birch-bark is resistant to fungal attack for a long time even at high humidity. These studies indicate that to prevent fungal growth, the best conditions for storage of the birch-bark manuscripts in museums will be at 20-25°C and 55-65% R.H. in a proper clean atmosphere. It is not necessary to have lower range of humidity. The birch-bark at low humidity tends to lose its flexibility. Furthermore, birch-bark has its own inbuilt resistance against fungus and it is not required to give any additional fungicidal treatment to it.

FUNGAL GROWTH ON BIRCH-BARK TREATED WITH DIFFERENT ORGANIC SOLVENTS

Various organic solvents, like acetone, ethyl alcohol, chloroform, toluene, etc. are often used in conservation laboratories for cleaning of birch-bark manuscripts. In order to ascertain if there was any inter-relationship of thus treated birch-bark manuscripts and the growth of fungus, some experiments were conducted. These experiments were necessary to have a standard for storage of treated and organic-solvent-leached birch-bark manuscripts. It was quite likely that the anti-fungal ingredient present in the birch-bark might get dissolved in the organic solvents, thereby exposing the birch-bark to the hazards of fungal growth at high humidity.

For experimentation, pieces of birch-bark were treated with different organic solvents, namely acetone, ethyl alcohol and chloroform and dusted with spores of A. niger (the test fungus) and placed at 100% R.H. and 28 ± 1°C temperature. A control set of birch-bark pieces without any treatment were also kept in the same manner.

The results obtained so far indicate that there was not much difference in the behaviour of the untreated and treated specimens. However, a definite conclusion cannot be drawn at this stage. Further work at varying temperature and humidity is required to be done in future.

USE OF BIRCH-BARK AS ANTI-FUNGAL AGENT

As it is seen from the earlier experiments, birch-bark does have an anti-fungal ingredient which resists the growth of fungus on it. Some experiments were conducted to ascertain whether birch-bark pieces or sheets can be used as anti-fungal agent for other objects, like paper manuscripts. Pieces of birch-bark and ordinary papers were placed together at 100% R.H. and 28 ± 1°C temperature for several days. Sets were also placed at ambient temperature and humidity. Observations were done at intervals. The results obtained so far are not very encouraging but further efforts are continuing in this direction.

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Table 1 Showing the growth of fungus on birch–bark and paper at different relative humidity, at 20°C

Days	Relative Humidity levels									
	100% B.B.	100% P.	85% B.B.	85% P.	75% B.B.	75% P.	64% B.B.	64% P.	52% B.B.	52% P.
4th	-	+	-	-	-	-	-	-	-	-
8th	-	++	-	-	-	-	-	-	-	-
12th	-	+++	-	-	-	-	-	-	-	-
16th	+	++++	-	+	-	-	-	-	-	-
20th	++	++++	-	++	-	-	-	-	-	-
24th	++	++++	-	+++	-	-	-	-	-	-
28th	++	++++	+	+++	-	+	-	-	-	-

Note 1 : Saturated salt solutions were used to get the desired R.H. Water : 100%; KCl : 85%; NaCl : 75%; NaNO2 : 64%; Mg(NO3)2 : 52%

Note 2 : B.B. in these Tables stands for Birch-bark and P. for Filter Paper.

Table 2 Showing the growth of fungus on birch–bark and paper at different relative humidity, at 25°C

Days	Relative Humidity levels									
	100% B.B.	100% P.	85% B.B.	85% P.	75% B.B.	75% P.	64% B.B.	64% P.	52% B.B.	52% P.
4th	-	-	-	-	-	-	-	-	-	-
8th	-	+	-	-	-	-	-	-	-	-
12th	-	++	-	-	-	-	-	-	-	-
16th	-	+++	-	-	-	-	-	-	-	-
20th	-	+++	-	+	-	-	-	-	-	-
24th	-	+++	-	++	-	+	-	-	-	-
28th	+	++++	-	+++	-	++	-	-	-	-

Note 1 : + = Poor fungal growth, ++ = Fair, +++ = Good, ++++ = Very Good growth, - = No growth.

2 : Control sets showed no fungal growth.

Table 3 Showing the growth of fungus on birch–bark and paper at different relative humidity, at 30°C

Days	Relative Humidity levels									
	100% B.B.	100% P.	85% B.B.	85% P.	75% B.B.	75% P.	64% B.B.	64% P.	52% B.B.	52% P.
4th	-	+	-	-	-	-	-	-	-	-
8th	-	++	-	+	-	-	-	-	-	-
12th	-	+++	-	++	-	-	-	-	-	-
16th	+	++++	-	++	-	-	-	-	-	-
20th	+	++++	-	+++	-	-	-	+	-	-
24th	+	++++	-	+++	-	-	-	+	-	-
28th	++	++++	+	+++	-	+	-	++	-	-

Table 4 Showing the growth of fungus on birch–bark and paper at different relative humidity, at 35°C

Days	Relative Humidity levels									
	100% B.B.	100% P.	85% B.B.	85% P.	75% B.B.	75% P.	64% B.B.	64% P.	52% B.B.	52% P.
4th	-	+	-	-	-	-	-	-	-	-
8th	-	+++	-	+	-	-	-	-	-	-
12th	-	++++	-	++	-	-	-	+	-	-
16th	+	++++	-	+++	-	+	-	-	-	-
20th	+	=	-	+++	-	+	-	+	-	-
24th	++	=	-	++++	-	++	-	-	-	-
28th	++	=	+	++++	-	+++	-	-	-	-

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