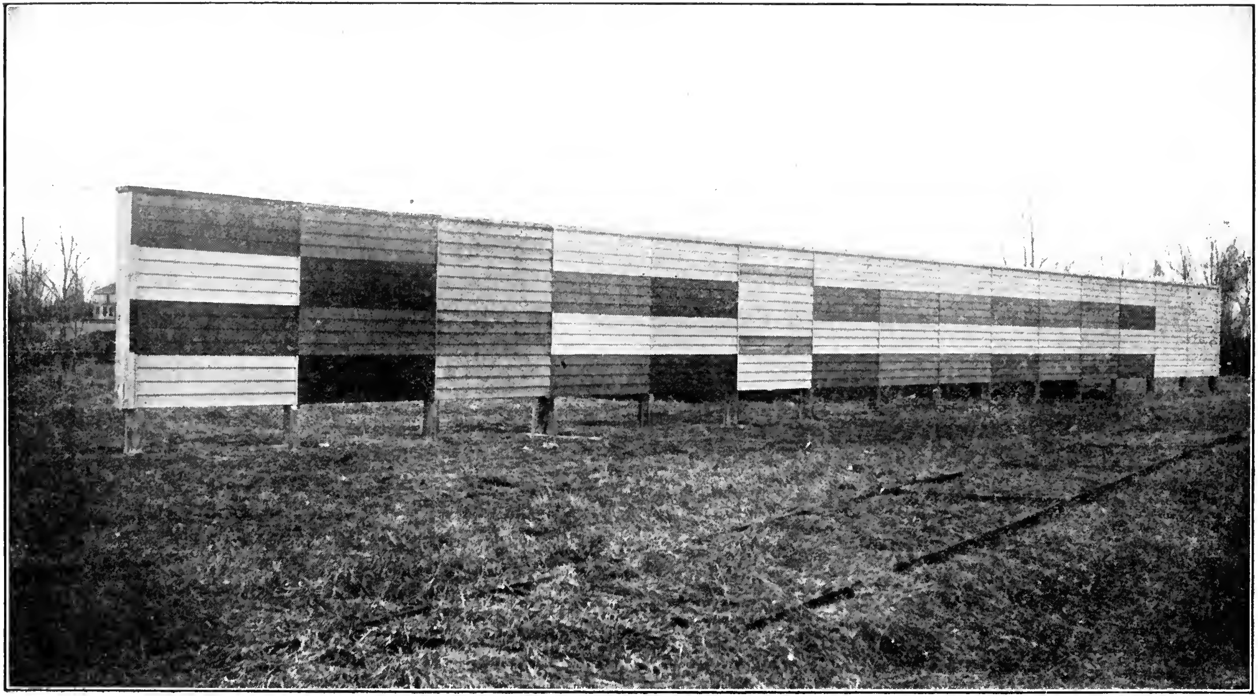

Frontispiece

ANALYSIS OF MIXED PAINTS, COLOR PIGMENTS, AND VARNISHES

BY

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PREFACE.

This book was written primarily to meet the needs of the author's own classes in Industrial Quantitative Analysis, and it is given to the public in the belief that there is a demand for a concise work on the analysis of paints and paint products.

Numerous books have been written during the past few years dealing with the subject of Paints, discussing in a general way the properties of the various pigments and their methods of manufacture. But the author is not acquainted with a single work that will serve as a guide to a chemist of ordinary training in taking a can of mixed paint, of practically any shade or tint, making a complete analysis of it and furnishing him sufficient data, derived from a large number of analyses, so that he may interpret the results of his own analysis in a rational manner.

It is the object of the author as far as may be to fill this much felt want, and the methods given in the following pages should be of interest to advanced college students who may wish to inform themselves on methods of paint analysis; to the industrial chemist who has more or less paint work to do; and especially to the young paint chemist who is just starting out in his career.

Each method given in this work has been tested out in the author's laboratory and its working value thoroughly demonstrated. The various analyses given are believed to be representative of the composition of the pigments they illustrate, and it is hoped that they will be of service in enabling the analyst to pass on paint products with fairness to both the manufacturer and the consumer. The chapters on varnish analysis are admittedly incomplete. Our present literature on varnish, and especially varnish analysis, is meagre, and much of it of a contradictory nature, but the author hopes in the near future to be able to present data that will be of further value to varnish chemists.

In conclusion the author wishes to express his sincere thanks to Commissioner E. F. Ladd for the portion contributed by him, and for his kindly guidance and interest in the entire work; and also to Mr. Clarence E. Kinney, who has assisted in much of the analytical work.

C. D. HOLLEY.

FARGO, N.D. *Feb. 19, 1907.*

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PART I.

READY MIXED PAINTS.

BY E. F. LADD.

ANALYSIS OF MIXED PAINTS.

READY MIXED PAINTS.

The rapid increase in the manufacture and consumption of ready mixed paints during the past third of a century has been quite phenomenal. To-day it is claimed that fully 70,000,000 gallons of paints mixed and ready for use are annually consumed in the United States. It is not strange, therefore, where without being placed under legislative restraint of any kind, in such a great industry and one so little understood by the general public, that abuses have arisen which will require courage, persistency, and legislative action to correct.

It is unfortunate that some of the mixed paints have so little of merit, and how are the public to separate the good from the bad? With competition so fierce as has been the case within the past few years, it is safe to say that paint manufacturers have not, as a rule, produced a paint as good as they knew how to produce, but rather that the best of them were making as good a paint as they could sell in the face of the kind of competition practised. There are many other manufacturers producing paint as cheaply as they can, and with little regard for wearing quality as a first consideration.

The writer maintains that a house well painted, primed and two good coats applied, should not require re-painting for protective purposes oftener than once in five to seven years. If every condition is favorable the paint may still be well preserved at the end of ten years. Not a few houses as now treated need re-painting at the end of two or three years, and not infrequently the old paint must be burned away before the new can be applied. Something is wrong where this is required, — not always the fault of the paints, sometimes the methods of application are faulty; conditions existing at the time of painting may be responsible for the trouble, or the paint previously used may be the source of the difficulty, and even the difference in the expansive properties in the two paints may be a cause for trouble.

In average conditions there is no valid reason why paints should ever crack, peel, blister, or pull away from the wood. It not infrequently does one of these, as well as show many other faults, all of which need to be understood and explained. A knowledge of the chemical and physical properties of the paint are the first essentials for understanding the reasons for these faults where the work has been well done. Why at times do paints crack, peel, scale, blister, or pull away from the wood, and do many other unreasonable things? Why in some instances will the paint wear well when the house is painted for the first time, and when re-painted with a different paint show many of these faults?

These and scores of other questions are asked by the general public, and they are demanding an answer. They are demanding an answer from those in whom they have confidence, and who, from their position, have no reason to become biassed. Our Experiment Stations must furnish this new sought for information. The chemist must acquaint himself with the subject, investigate, experiment, keep in touch with the processes of manufacture, and aid the consumer in arriving at a rational explanation. He must go farther, and know paints. The paint manufacturer's chemist can do much, but he is usually an interested party, and a more searching investigation is required than he can command time or means to give to the problem. There is needed such investigation as only well-equipped experiment stations can command for such a study.

The North Dakota Experiment Station has undertaken this line of work, and has erected several experimental paint fences of the type shown in the frontispiece of this book, as well as undertaking to conduct paint tests on a broad scale upon a number of buildings, employing various combinations of pigments. These tests will be continued for a series of years; and frequently repeated and the whole question studied, in order to determine what is best with conditions such as exist in North Dakota and like adjoining territory.

Let us not be too severe in our criticism of the paint manufacturer until the full truth is known, and this as the results of honest investigation. No man can prevent the dishonest use of data given to the public in the best of faith and when rightly used of great value, but in the hands of dishonest salesmen distorted and abused. The methods of salesmanship usually, however, reflect the true character of the house behind the men, and therefore are beacon lights not to be wholly ignored.

At the present time nearly all families are users of paints, nevertheless but few persons are familiar with the composition or working qualities of paints. There are few subjects of greater importance to the builder, since the appearance of a building is to be judged largely by the character of the finishing coat, which is paint. And yet how little the average person knows of the subject of paints. Nearly all would be able to tell you something concerning building materials, cements, methods of construction, and would recognize good work in any of these lines, but few know the composition or properties of paints used to give the finishing coat and proper protection to the walls of our homes. Only a limited number would be able to intelligently criticise the work. That some paints wear well, some crack or aligator, others peel and some blister, while others chalk, is generally recalled, but the reason for this is not considered. The average property owner from the East will tell you that the paint on buildings does not wear like it formerly did, and they wonder why. Is it, they say, because of the inferior quality of the white lead used at the present time, or because of poor workmanship? They do not consider that there are many other factors which may have entered in as a cause for present existing conditions, among which may be mentioned, the inferior character of some of the wood now employed for sidings; the condition of the wood at the time the paint is applied which may be unfit to receive the coat of paint. Or it may be due to the character of the priming coat which was of inferior quality, perhaps a low grade of ochre, wholly unfit to be used as a primer. Even the character of the oil not properly ripened, etc., may be a determining agent. It may be due in part to the physical condition of the paint, for it is a well-known fact that there are now on the market numerous paints, the physical condition of which cannot be commended, certainly not if, as has been claimed, that fineness is an essential for good wearing quality. More often it is due to the character and condition of the adulterants which are added to the paint, for it cannot be denied but what some of the products in the proportion in which they are added, whatever their individual merits may be, can only be looked upon as adulterants. Or it may be due to the presence of an excessive amount of water used in the paint, for many of the paints which have been sent out of late years have contained unnatural proportions of water, — not intended to add value to the paint, or to serve for preventing its settling and hardening. Not more than from one to two per cent of water is needed, if at all necessary, for this purpose. It is not uncommon for paints to contain from ten to twenty-four per cent of water in the liquid portion. This, with the small amount of added alkalies and jelly-like constituents, has produced serious results for the paint consumer. Excessive quantities of benzine, kerosene, gasoline, and various other thinning vehicles have likewise, been a source of trouble.

What is needed first of all, is a better acquaintance with the whole question of paint manufacture and use. The first essential is that the public should become acquainted with the chemical composition of paints: having made themselves acquainted with their composition, they will then know whether the products purchased are what they are represented to be. They will then need to become familiar with the physical properties of paints, and their working qualities under the brush. This will then naturally lead to a study of paints upon buildings, and the public will become familiar with their wearing qualities; thus they will be able to understand some of the causes which lead to the deterioration of paints, and they will then demand products of far better quality than much of that which has been sent into the state in the past, even by some well-known firms.

It is true that competition has forced honest manufacturers to lower their standards so that they are producing paint not as good as they know how to produce, but as good as the general public are willing to pay for in the face of existing competition with unscrupulous manufacturers and catalog house goods, which have fast forced down the standard of products in all lines handled by department stores and run as money-making ventures.

North Dakota was the first state to enact any comprehensive measure affording protection to the public against abuses not uncommon during the past few years.

The essential features of the North Dakota paint law are found in Section 1, which reads as follows:

"SECTION 1. Every person, firm or corporation who manufactures for sale or exposes for sale, or sells within this state, any white lead, paint or compound intended for use as such, shall label the same in clear and distinct gothic letters upon a white background and show the true per cent of each mineral constituent contained in said paint, or if other than linseed oil is used in its preparation, the names of such oils or substitutes shall be shown together with the percentage thereof, and every person, firm, or corporation who manufactures for sale or exposes for sale, or sells within this state any mixed paint or compound intended for use as such, which contains any ingredients other than pure linseed oil, pure carbonate of lead, oxide of zinc, turpentine, Japan drier and pure colors, shall be deemed guilty of a misdemeanor, and upon conviction thereof shall, for each offence, be punished by a fine of not less than twenty-five and not more than one hundred dollars and costs, or by imprisonment in the county jail not exceeding sixty days; provided, that any such person, firm or corporation who shall manufacture for sale or expose for sale, or sell within this state any white lead, paint or mixed paint containing ingredients other than those as above enumerated, shall not be deemed guilty of a violation of this act in case the same be properly labelled, showing the quantity or amount of each and every ingredient used therein and not specified above, and the name and residence of the manufacturer or person for whom it is manufactured."

Like many first laws there is considerable ambiguity and an opportunity for misinterpretation of the spirit of the law. It is true also that the measure has been attacked on the ground of unconstitutionality, and a decision has not as yet been reached by the highest court in the land, and cannot be for some months yet, although the constitutionality of the act has been affirmed by the United States District Court for North Dakota.

The North Dakota law does not require paints made wholly from commercially pure white lead, zinc oxide, linseed oil, turpentine, Japan drier, and pure colors, to be labelled. All other paints must be labelled so as to show their true composition.

There has been a difference of opinion as to whether a law regulating the sale of paints should require all paints to be labelled, or only those which have departed from the constituents which have been long recognized as the basis for paint manufacture. Many arguments have been put forth to show that a law exempting any paints is unfair, but the evidence thus far presented has not been sufficient to show that it would be desirable at this time to recommend any change in this direction. It is true that all of the so-called inert materials have been used and are still used to some extent in the various mixed paints, but the paints containing these constituents have generally been represented as being produced wholly from the constituents recognized as statutory, and thus the manufacturers have themselves made this natural and distinctive classification which has been adopted in the North Dakota law.

The pigments which have been used as substitutes are divided into two groups. The first group includes chalk, mineral white, barytes (natural or artificial), gypsum, silicates, calcium carbonates under various names, as Spanish white, English white, marble dust, Paris white, whiting, etc.; magnesia compounds, and various alumina products, as, for example, China clay.

The second group includes sublimed lead, lithopone, leaded zinc, and zinc lead white.

It may be conceded that products of the first group are possessed of merit for certain purposes, yet they have been most generally employed as adulterants, and are found, possessed of inferior quality, to the greatest extent in low grade paints, or as adulterants for white lead. They are cheap, therefore lend themselves to misuse.

It is not generally claimed that they are substitutes for white lead in oil, but rather that they can be used in combination with white lead within certain limits and, at times, with advantage. There is, however, no general and fixed consensus of opinion among paint manufacturers or their chemists as to which of these are best, — some manufacturers condemning one and extolling the merits of another, while a competitor will as vigorously contend that the reverse is true.

The physical condition of the pigment is often a controlling factor, for it is now well recognized that fineness of subdivision of pigment is of vast importance. Again, not all of the products sold under a given name are of like value, or even of like chemical composition. This is well shown in the case of gypsum, much of the Western gypsum being of inferior quality and not the equal of certain Eastern products. If the gypsum is not properly dehydrated then, in the presence of moisture as found in paints, a serious difficulty arises. Or if lime carbonate be present then by the dehydration of the gypsum quicklime is produced and causes complications. It has been asserted also that lime carbonate is desirable to counteract any acid properties in the oil, but it may be asked why will not the white lead or even zinc oxide serve the same purpose?

Such arguments seem futile, and certainly if any advantage is to accrue from the use of chalk or marble dust over that of lead or zinc, not to exceed two per cent would be required and the necessity for the presence of any great amount of a neutralizing agent at once raises a doubt as to the value of the linseed oil, — that is, as to its freedom from oil produced from foreign seed, and to its proper aging, or, if boiled oil, its method of preparation.

With the present confusion and lack of unanimity among paint chemists and manufacturers as to the relative merits of the constituents and the very general belief that the pigments of group one are largely employed as cheapening agents, and not always to the advantage of the purchaser, we may dismiss for the present any consideration of their being the equal of the statutory pigments in ready mixed house paints; at least until such time as their true worth has been demonstrated through a rigid and comprehensive series of practical paint tests checked up by appropriate chemical and physical examinations. It will also be necessary to determine to what extent, if any, they can replace white lead, or should the proportion of white lead remain the same and they be used as a substitute for the zinc oxide.

It should not be understood, however, that these products when properly used are to be classed as adulterants, for this term is being abused and misused. For example, in lithopone, barium sulphate is a recognized component, and when lithopone is used as such it is a perfectly legitimate product. The same is true of many other pigments.

With regard to the members of group two, some discussion of the several pigments will not, at this time, be inappropriate.

Sublimed lead. Sublimed lead sulphate, sometimes called the oxy-sulphate, or the basic sulphate, seems to have had many ups and downs in its short history.

It was first put upon the market commercially about twenty-five years ago and, according to Hurst, its composition was very variable, much depending upon the character of the low grade ores from which it was produced, the temperature in the furnace, and the proportion of air which came in contact with the ore. Writing as late as 1901, Hurst reaffirms his former statement with regard to its variable composition. Many of the manufacturing obstacles have, however, been largely overcome in the last few years, especially in America, and the product is now tolerably uniform, and in the purest form seems to average in composition about:

	Per cent.
Lead sulphate	75
Lead oxide	20
Zinc oxide	5
	100

The pigment is very fine, possessing good covering power, but in use is not always satisfactory. Sublimed lead seems to differ in many ways from the simple physical mixture of lead sulphate, lead oxide, and zinc oxide. The claim that it is the basic sulphate, or the oxy-sulphate, seems, however, not to have been properly verified at the present writing. It seems to be rather a complex mixture of several of these constituents. That it should differ from a mechanical mixture of the above-named pigments, may be due in part to the greater degree of fineness and more complete intermixture in the process of sublimation.

The use of sublimed lead has greatly increased during the past few years, and an increased number of manufacturers are now using sublimed lead to some extent. In the preparation of mixed paints the firms adopting its use to the largest extent during the past two years, judging from the paints sold in North Dakota, are the ones least equipped for conducting experimental work under the guidance of a trained chemist.

Several firms report having in years past tried the product with unsatisfactory results, and have discontinued its use in their regular lines of mixed paints. Firms who have been using sublimed lead in their darker shades have not generally adopted its use in the whites. However, in one instance when used with a white this yellow tint was corrected by the addition of a slight amount of blue.

For example, a gray and an outside white as examined gave for the essential constituents approximately as follows:

	White.	Gray.
White lead	59.00	9.00
Lead sulphate	2.00	45.00
Zinc oxide	34.00	44.00

There has been considerable complaint regarding the working qualities of sublimed lead paints. In a test made by using sublimed lead ground in oil and with great care to prevent heating, it was found that during the cool part of the day, in the morning and evening, the paint was spread and brushed out with considerable difficulty. Others have reported like experiences. In a more recent test, where a mixed paint composed of 60 per cent of sublimed lead and 40 per cent of zinc oxide was under test, considerable difficulty was experienced toward evening as the day became cooler, although all the other conditions were most favorable for painting.

In the past there has been produced a large number of paints of rather inferior quality, so far as composition is concerned, made up largely of so-called inert material: chalk, barytes, clays, silicates, water, etc., and it is notice-able that during the past two years, or since the enforcement of the North Dakota law, several of these firms have been endeavoring to improve somewhat the quality of their paint, and are substituting sublimed lead or lead sulphate, but even in the best grades of these paints, as examined in this laboratory, it has been found that the lead sulphate is generally used in combination with other products and particularly with white lead proper, and not alone or with zinc oxide only.

An example of the change made in one case is clearly shown by comparison of an outside white as produced one year ago, with that produced by the same firm at the present time:

	Old.	New.
Lead sulphate	0.00	20.00
Zinc oxide	53.00	43.00
Calcium carbonate	46.00	26.00
Silica	...	11.00

For the new product, it is claimed on the label that the formula is:

	Per cent.
Zinc white	55
Lead white	45
	100

This is not at all what the analysis shows it to be.

In the case of another sample of paint recently examined we find the proportion to be:

	Per cent.
White lead	23
Lead sulphate	19
Lead oxide	6
Zinc oxide	26
Barium sulphate	22
Other constituents	4
	100

A mixed paint to be satisfactory must not be too slow in drying, otherwise showers, dust storms, and myriads of insects deface it and give an unsatisfactory surface. The tendency for a paint to become gelatinous is also an unfortunate condition at times met with. These last named properties have been objections strongly urged against the use of sublimed lead. When used in connection with considerable proportions of white lead, zinc oxide, and diluting materials, or inert pigments, it is possible that sublimed lead may give satisfactory results, and this would seem to be true since we have found its use more general under these conditions, also in cases where permanent whiteness is not such an important matter. From personal knowledge the writer would say that sublimed lead is better adapted for use in paints for farm machinery, where dipping is resorted to rather than brushing.

Lithopone. Lithopone is now a fairly uniform product, quite generally used in the preparation of the cheaper enamels, in oil cloth, and floor cloth industries and, to some extent, in floor paints, but it has not, as yet, been used to any great extent in mixed paints. From its nature it cannot be used in paints under certain conditions with any degree of satisfaction, and, therefore, the purchaser should know of its presence in order that he may avoid such difficulties. Aside from any objectionable features it is probable that the demand for lithopone for other purposes will be such as to prevent its being generally employed, for some time at least, in the preparation of mixed paints except in certain specialties.

Leaded zincs. Leaded zincs show considerable variation as now found upon the market. The New Jersey zinc produced from Franklinite is practically 99 per cent or more zinc oxide, and seldom contains more than a trace of lead. On the other hand, the Mineral Point zinc contains varying amounts of lead sulphate, and above all zinc sulphate which is recognized as an objectionable feature when present in any considerable quantity.

There would seem to be three grades of Mineral Point zinc products, the purest of which contains from three to four per cent of lead sulphate.

The leaded zincs from the Missouri and Kansas fields show an extremely wide range in composition, containing from four to twenty-five per cent of lead sulphate, and, at times, as high as one and a half per cent of zinc sulphate. It also at times contains as high as one-half per cent of SO_2 which in some instances in paint manufacture has been a source of great trouble, resulting in heavy loss and in the production of a paint not usable.

With regard to zinc sulphate, Hughes says: " Zinc sulphate, an almost invariable ingredient of leaded zinc, and zinc oxide made from sulphides sometimes causes startling changes for which the painter usually is blamed."

In the light of present experience, therefore, zinc sulphate in such quantities cannot be looked upon other than with some degree of suspicion in mixed paints, although Toch does not consider it harmful to the extent that has been generally claimed.

It would seem, therefore, that before one is justified in assuming the presence of zinc sulphate as without prejudicial influence, it will be necessary to conduct investigations in practical tests to determine under what conditions, if any, it can be safely allowed in paints, and to what extent.

Zinc lead whites. Zinc lead white is largely a product from Colorado low grade ores, — a mixture of zinc oxide and lead sulphate very intimately combined at the high temperatures at which these products are volatilized, and then are oxidized in appropriate chambers. Only during the past five years has there been attained anything like uniformity in composition and, even at the present time, as shown under the analyses of zinc lead whites by Professor Holley, they have been found to contain the following range for arsenic, antimony compounds, and zinc sulphate:

	I	II	III	IV
	Per cent.	Per cent.	Per cent.	Per cent.
Arsenious oxide	.68	.47	.32	1.60
Antimony oxide	.20	.33	.20	.88
Zinc sulphate	.78	.55	1.61	.84

In other words there may be present as much as three and one-half per cent of these objectionable constituents. The writer seriously questions whether the presence in these proportions of such constituents does not very materially detract from the good quality of paint. Certainly arsenic and antimony compounds are not more desirable for interior paints than are the arsenic compounds desirable in our wall papers, the presence of which in wall paper in the past has proven such a menace to health.

The writer cannot do other than maintain that when any of the foregoing pigments are used in place of the long recognized statutory pigments, the public have a right to know of their presence, and they are not to be classed as possessed of the same degree of merit for paint production as are the statutory pigments. At least it cannot be claimed that experience has, as yet, demonstrated their like worth. Further, the fact that the manufacturer of those pigments is constantly striving to eliminate certain constituents; adopting new devices in manufacture, and bringing out new products and presumably better than that previously produced, is indicative of needs for further improvements and clearly indicates an unsettled condition.

If there are standards recognized for food products, for drugs, for beverages, such as whiskey, for commercial fertilizers, etc., why should not like standards, generally recognized from their long and favorable use, be accepted as a basis for paints of high quality? Any attempt, therefore, to secure legislation requiring all paints to be labelled under like conditions is an attempt to place all constituents entering into the composition of paints on a like footing. Every honest paint manufacturer knows that such claim is not true.

In dealing with this question the writer would have it understood, of course, that his reference has been to that class of mixed paints used as house paints, and not those special paints prepared for use upon structural steel, for lighthouse purposes, or even upon railway cars, where conditions are quite different, and where, as a rule, expert chemists are employed to see that the products furnished are in compliance with previously prepared specifications, none of which conditions pertain to paints as ordinarily met with in commerce. Otherwise, who is to safeguard the consumer against such abuses, or how is the producer of honest paints to have proper protection?

Under the North Dakota law it is required, where constituents other than statutory ones are employed, that the paint shall be labelled to show the composition of the same, and the form which presents this information most satisfactorily for the public, it seems to the writer, is the one adopted in reporting the analyses made at the North Dakota Experiment Station, and is as follows:

FORM FOR LABEL.

	gal.	lbs.
Contents of can		
Per cent of pigment, by weight	62	
Per cent of thinner or vehicle by weight	38	
	100	

The thinner or vehicle is composed of:

	Per cent.
Linseed oil	70
Turpentine	5
Japan drier	5
Benzine	10
Water	10
	100

Composition of pigment:

	Per cent.
White lead	25
Sublimed lead	20
Zinc oxide	30
Calcium carbonate	6
Barytes	15
Color [1]	4
	100

This should be followed or preceded by the name of the manufacturer and his address. This does not preclude however, the use also of the name of the jobber on the same label if it is desired.

Where water is present not to exceed 1.5 per cent of the fluid portion it is considered as incidental. Or where Western zincs are employed and carry not to exceed 5 per cent of lead sulphate, and are free from other injurious impurities, the products are considered as commercially pure and labelling is not necessary, provided all other conditions are in compliance with the requirements of the law.

[1] The color is composed of: (name of ingredients and composition when necessary to be given.)

Where coloring matter is used to secure the desired tint, it is assumed that this coloring matter is commercially pure, but where the coloring matter is of such a character as to require an unusual amount of color, then the product should not be deemed as properly labelled unless the analysis of this color be given. It is a well-known fact that some of the ochres are of such inferior quality that not less than 20 per cent of the color may be used as pigment, and not more than 8 or 10 per cent of this should properly be classed as real color, and the other constituents enumerated as dilutants.

The question may be raised as to the reasons for labelling as indicated in the foregoing. It will be observed in the study of paints that the manufacturer who uses the largest amount of cheap, inferior pigments will employ the least amount of oil, for when calculated according to volume, oil is more expensive than some of the pigments. He, therefore, adds water and recommends that the consumer add the necessary oil and turpentine to thin the same for use. On the other hand, the manufacturer producing the highest grade of paints tries to combine pigment and vehicle in such proportion that they are ready for use; but linseed oil is cheaper than white lead, and, therefore, some paint manufacturers employ as large a per cent of oil as can well be used, and advertise the great spreading power of their paints.

It is thus important that we have full measure or weight, and proper information with regard to the proportion by weight of pigment and thinner.

By separating the thinner or vehicle from the pigment, the facts are most clearly indicated to the untrained mind, for example, the proportion of water; for instance, ten pounds in every hundred of the liquid portion. Or in the pigment thirty pounds of chalk or marble dust or barytes to each hundred pounds. Where the pigment and vehicle are combined the relative proportion of barytes, benzine, water, etc., is made to appear considerably less than where they are calculated on the actual amount of thinner employed, and this to the advantage of the manufacturer.

To make a statement for the express purpose of misleading, is as much a falsehood as to deliberately tell a lie, and indicates that there is back of it, one not wholly to be relied upon in matters upon which he should be an authority.

To say that the lead and zinc in the paint are "guaranteed to be strictly pure," when they constitute but part of the pigment, is to perpetrate a fraud, and to deliberately falsify. Yet this is not an uncommon practice in regard to paint literature furnished by manufacturers. Or, if not found in the literature, it is spoken by the salesman who represents the product.

Take this statement: "This mixed paint contains the proper proportion of zinc. It is a lead, zinc, and oil paint — the real thing." Is this a truthful statement when the composition is:

	Per cent.
White lead	25
Lead sulphate	25
Zinc oxide	25
Barytes	25
	100

No honest manufacturer of paints should make a statement like the foregoing, or allow his salesmen to misrepresent facts. And yet if you are to eliminate all as friends who follow such a course, there would remain but few manufacturers for one to associate with. Such ingenious statements do not give one a good opinion of business men engaged in the manufacture of paints, and if their word is questioned on paint matters they have no just reason for resenting it, until such time as paint literature is properly revised. Commercial practise rather than inherent dishonesty is at fault, for much of this unfortunate condition, also lack, on the part of some manufacturers, of moral courage to lead in a crusade for honest labelling. Time and forced changes must soon remedy this condition.

Here is another example of fraud, — where the manufacturer labels his product as " white lead " and says: " We guarantee our white lead to be superior to any white lead on the market as regards opacity or body-covering capacity. It is also extremely durable, possessing in this particular great merit. For whiteness and fineness of texture it will be found unsurpassed." Now he has told but a small part of the real truth.

Now the public are justified in believing that this product is the equal of any white lead upon the market. In fact, that it is chemically pure white lead. The analysis shows the pigment to contain:

	Per cent.
White lead	37.51
Lead sulphate	7.84
Zinc oxide	25.87
Calcium carbonate	20.36
Barytes, silica, and undetermined	8.42
	100.00

Another product labelled as white lead was found to contain 90 per cent of barytes, and no white lead at all.

Now such claims as the foregoing are intentionally misleading and false, are given out solely for the purpose of deceiving the public, and inducing them to purchase these products at exorbitant prices. These products usually retail at about the same price as does genuine Old Process Dutch White Lead, and it is to secure this unwarranted advantage that many of these products are so advertised.

As showing the need of: a law to prevent fraud in paints we may cite a few examples. We give three analyses of products sold as white lead and usually at approximately the same prices per pound as received for Old Process Dutch White Lead.

	No. 1.	No. 2.	No. 3.
White lead	00	00	39
Lead sulphate	20	5	5
Zinc oxide	20	25	34
Calcium carbonate	8	..	19
Barytes	52	70	3

Many manufacturers dwell much upon the importance of having pure linseed oil and turpentine, and maintain that the life of the paint is largely dependent upon the linseed oil. Some of the paints found upon the market in North Dakota at the time the law went into force, clearly shows a kind of "doping" not at all commendable or in keeping with what the public had a right to presume they were purchasing.

We cite the following examples as showing the composition of the liquid portion of some of these paints.

	1	2	3	4	5	6	7
Linseed oil	55	69	52	70	57	72	64
Turpentine	..	..	..	11	..	..	6
Benzine	24	16	26	..	21	4	14
Water	21	15	22	19	22	24	16

This certainly shows a remarkable condition, and one which all paint chemists have condemned, and yet this represents not alone the low grade paints, but some of the products produced by manufacturers of the highest standing.

As to the use of water in paints, without further comment we may quote Toch: "Three per cent is entirely excessive in an exterior linseed oil paint, and a manufacturer has no right, either morally or legally, to hide behind a misrepresentation of his paint when the paint is largely adulterated for the purpose of overcoming his ignorance in the manufacture."

That the water further exerts an injurious effect is also noted by the same author, who says: "Ethics would clearly indicate that no manufacturer has a moral right to label his paint as being entirely pure and composed of four materials, when as a matter of fact an excessive quantity of water was added which destroyed in a large degree the value of the other materials."

On the other hand, as showing about the proportion of the constituents entering into the fluid portion of some of the best made paints, we quote the following example:

ANALYSIS OF THINNER.

	1	2	3	4	5	6
Linseed oil	93	91	86	95	90	94
Turpentine drier	7	9	14	5	10	6
Water	0	0	..	0	0	0
Benzine	0	0	0	0	0	0

In the best prepared paints we have usually found from 4 to 7 per cent of turpentine drier in the liquid portion. For a heavy-bodied oil this seems to be ample.

Without entering into any further discussion as to the relative merits of the various pigments we may consider a few cases where the public were justified in assuming they were purchasing a paint made wholly from white lead and zinc oxide.

ANALYSIS OF PAINT PIGMENTS.

	1	2	3	4	5	6
White lead	00	9	00	00	00	00
Zinc oxide	53	44	40	24	47	43
Calcium carbonate	46	..	34	5	..	26
Magnesium carbonate	1	..	..	..	..	..
Barytes	..	..	22	66	..	..
Lead sulphate	..	45	4	5	3	19
Clay and silica	..	2	..	..	49	12

Without commenting on the physical condition of these several paints which in some instances were not at all desirable we may ask: Is the public not entitled to some protection against the sale of paints so labelled as to give the impression that they are getting white lead and zinc oxide? Not all of the above paints are by any means to be classed as catalog house paints. It is not for one moment to be supposed either, that the paints are ideal in composition or that the honest paint manufacturer so considers them.

Here is a type of a different class of paints put up in dry form and largely advertised.

	Per cent.
Moisture and combined water	5.74
Casein	14.59
Ferric oxide	19.26
Soluble alumina	1.24
Gypsum	21.53
Lime	7.60
Magnesium silicate	30.04
	100.00

The constituents other than casein in this costs about one cent per pound, and it is a good example of what might properly be classed as a " fake " paint.

If a cheap paint is desired it is better to use a good whitewash, for it would probably serve as a protective coat better than the above. What is known as the Government formula for whitewash is as follows:

" Slack one-half bushel of lime with boiling water, keeping it covered during the process. Strain it, add a peck of salt dissolved in warm water; three pounds ground rice put in boiling water and boiled to a thin paste; one-half pound powdered Spanish whiting, and a pound of clear glue dissolved in warm water; mix these well together and let the mixture stand for several days. Keep the wash thus prepared in a kettle or portable furnace, and, when used, put it on as hot as possible with painter's or whitewash brush."

Short measure and weights. Another feature quite common is short measure in mixed paints and short weight in paste paints. In case of white lead and combination leads they average 10 to 12 per cent short weight, or kegs sold for 12½ pounds will run 10 to 10½ pounds, and 25 and 50 pound kegs, respectively, about 22 and 46 pounds. All weights should be net as represented.

In the mixed paints they run not infrequently 10 to 13 per cent short in measure. In two-quart containers we have found them to run as follows:

Number.	Quarts.
1	1.92
2	1.82
3	1.76
4	1.75
5	1.70

One of the gallon containers purchased direct from the producer actually contained 3.41 quarts.

Relation of lead to zinc. Much has been said concerning the fact that the North Dakota law is silent regarding the proportion of lead to zinc permissible in statutory paints. Who shall at the present time say what proportion is best? The relation of lead to zinc for exterior work would undoubtedly be different than in paints intended for interior house painting. The difference in cost between the best grades of those two pigments is not so great that manufacturers of high grade paints will be likely to cheapen the product at the expense of what to him seems safe for the locality where his paint is most largely used. At the present time we find that some are using 30 per cent of white lead to 70 of zinc oxide. This is the limit for zinc. Others employ these in proportion of 50 per cent for each, and there are now a few using 60 per cent of white lead and 40 per cent of New Jersey zinc oxide.

There are many practical painters who express the opinion that the proportion should be from 66 to 75 per cent lead, or not more than one-fourth to one-third of the pigment should be zinc oxide, while the advocate of white lead would have none of zinc. A few of the white lead advocates would use 10 to 25 per cent of zinc oxide in the finish coat. Experiments are necessary to determine in what proportion these pigments shall be added in order to secure the best results.

Experience may teach us that some of the other pigments are preferable to either of the above named. If so, we should welcome the proof and prepare to adopt standards of comparison based on such proof. The author is a believer in mixed paints, but maintains that when other constituents, either as thinner or pigment, are introduced in place of those generally recognized as being present, this fact should be clearly set forth and that false or exaggerated statements regarding all claims of paints should be discountenanced alike by the general public and the honest manufacturer, who in the past has suffered through abuses of commercial methods based upon an erroneous idea of the science of right and of right character and conduct in business affairs. In the end, in paint matters as well as elsewhere, that which is true and just will prevail.

PART II.

ANALYSIS OF PAINTS, COLORS, AND VARNISHES.

BY C. D. HOLLEY.

CHAPTER I.

ANALYSIS OF MIXED PAINTS.

1. **Preparation of sample.** If a dry color, and in bulk, great care must be exercised in securing a *uniform sample* which should be thoroughly mixed on the mixing cloth. If the sample be a liquid paint in the unbroken package, the brand, manufacturer, and guarantee should be carefully noted. The package is then weighed, opened, and the condition and volume of the contents noted. If the pigment has settled hard in the bottom of the can, pour off the oil into the mixing can and work up the paste until free from lumps, gradually adding the oil portion and stirring to a uniform consistency; pour into the mixing can, scraping out the contents of the package thoroughly. Stir until thoroughly convinced that the sample is *uniform in composition.* The entire success of the analysis depends upon securing a uniform sample, and more analyses are incorrect because of carelessness in the preparation of the sample to be analyzed than from any other source. The volume and weight of the empty can are also noted.

2. **Separation of the vehicle from the pigment.** Much difficulty is often experienced in extracting the vehicle from the pigment, due to the fineness of the pigment particles and the ease with which they pass through the walls of the extraction tubes. This difficulty, however, may be entirely avoided by the use of the apparatus illustrated below. The extraction thimble, containing a filter folded cylindrically, is dried in the hot water oven for one hour, weighed, and 10 to 15 grams of the sample weighed into it,

extracted with ether for 24 to 36 hours, dried and weighed again. The loss in weight represents the vehicle, and the residue remaining, the pigment, which is reduced to a fine powder and kept tightly stoppered until examined. Any

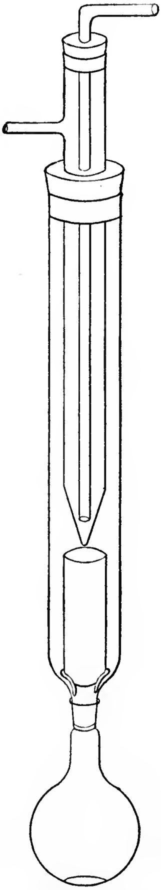

FIG. 2. — EXTRACTION APPARATUS.

casein or similar product in the paint will remain unextracted by the ether, and unless detected will interfere with the proper analysis of the pigment.

3. **Ratio of pigment to vehicle.** It is customary with a large number of manufacturers to have one ratio of pigment to vehicle for white paints, and another ratio for the tints. In some cases this is necessary, owing to the low specific gravity of the tinting colors; but in many instances where only one or two per cent of color is added to the white base, it is not necessary to reduce the proportion of pigment, even though such paints may hide better than the whites.

4. Typical analyses of white and gray paints, from the same manufacturers, showing the change in the ratio of pigment to vehicle.

	I.		II.		III.	
	White.	Lead Color.	White.	Gray.	White.	Gray.
Pigment	65.6	57.2	62.6	54.9	63.2	54.9
Vehicle	34.4	42.8	37.4	45.1	36.8	45.1
	100.0	100.0	100.0	100.0	100.0	100.0
Vehicle:						
Linseed oil	88.9	89.5	86.0	84.7	97.0	83.9
Drier	9.3	8.6	12.6	13.8	2.0	14.9
Water	1.8	1.9	1.4	1.5	1.0	1.2
	100.0	100.0	100.0	100.0	100.0	100.0
Pigment:						
White lead	14.65	14.18	44.08	27.29	50.52	33.98
Lead sulphate	0.34	0.27	4.62	4.39	0.00	2.84
Zinc oxide	63.42	63.27	41.41	50.94	46.06	41.80
Calcium carbonate	...	...	4.59	7.10	3.18	6.94
Silica	20.91	20.14	...	...	...	12.14
Magnesium silicate	...	...	5.10	6.94	...	...
Undetermined, color, etc.	0.68	2.14	0.20	3.34	0.24	2.30
	100.0	100.0	100.0	100.0	100.0	100.0

Analyses by the author.

5. **Composition of colored paints.** After the extraction of the vehicle it is necessary to examine the pigment qualitatively in order to ascertain the ingredients to be determined. The usual qualitative scheme may be followed with advantage. The colors as given on the color cards of paint manufacturers are usually confined to a limited number of combinations, the possible components of which may be easily ascertained, and which, in fact, are usually well known to paint chemists; but to the chemist who has had but little experience along paint lines, the following tables of color ingredients will be of interest. Unfortunately, manufacturers are not agreed among themselves as to standards for naming colors; for example, a tea green put up by one manufacturer may not correspond with a tea green put up by another; but by a careful study of the color cards issued by reputable paint manufacturers, it is usually possible to identify the color to be analyzed. Also the same or closely the same color may be produced by different combinations of color pigments, hence it is necessary to state all of the possible constituents that may be used, as far as the author has been able to ascertain them, even though it is quite probable that they may not all be present in the same paint.

6. **Reds:**

Brick. Base white, ochre and Venetian red.
Flesh Color. Base white, ochre, Venetian red, and sometimes orange chrome yellow.
Indian Red. Indian red.
Lilac. Ultramarine, carmine, Indian red, ochre, lampblack.
Maroon. Carmine, ultramarine, lampblack, Tuscan red.
Pink. Base white, orange chrome yellow.

Terra Cotta. Base white, burnt sienna, umber, chrome yellow, Venetian red, ochre.

Salmon. Base white, vermilion, lemon chrome yellow, sienna, ochre, Venetian red, orange mineral.

Tuscan Red. Tuscan red, Indian red, Para vermilions.

Venetian Pink. Base white, Venetian red.

Venetian Red. Venetian red.

7. Blues:

Azure Blue. Base white, ultramarine blue, chrome green, Prussian blue.

Bronze Blue. Black, Prussian blue.

Dark Blue. Base white, chrome green, Prussian blue, ultramarine, black.

Light Blue. Base white, ultramarine, Prussian blue.

Neutral Blue. Base white, Prussian blue, umber, black.

Robin's Egg Blue. Base white, ultramarine, lemon chrome green.

Sky Blue. Base white, cobalt blue, Prussian blue, ultramarine blue, chrome yellow.

8. Yellows:

Buff. Base white, ochre, black, red chrome lead.

Canary. Base white, lemon chrome yellow, chrome green.

Citron. Base white, Venetian red, Prussian blue, chrome yellow.

Cream. Base white, ochre, Venetian red.

Deep Cream. White, ochre, Venetian red.

Ecru. Base white, ochre, chrome yellow, black, chrome green.

Ivory. Base white, chrome yellow, ochre.

Lemon. Base white, chrome yellow.

Manilla. Base white, ochre, chrome yellow.

Stone. Base white, ochre, umber, chrome yellow.

Straw. Base white, chrome yellow, ochre, Venetian red.

9. Greens:

Ivy Green. Ochre, lampblack, Prussian blue.

Light Green. White, Prussian blue, chrome green.

Manse Green. Chrome green, chrome yellow, ochre.

Moss Green. Base white, ochre, chrome green, lampblack.

Olive Green. Lemon chrome yellow, ochre, ultramarine blue, Prussian blue, Indian red, chrome green, lampblack.

Pea Green. Base white, chrome green, very rarely emerald green.

Sap Green. Base white, chrome yellow, lampblack, chrome green.

Sea Green. Base white, chrome green, sienna, ochre.

Tea Green. Base white, chrome green, chrome yellow, lampblack.

Willow Green. Base white lead, chrome green, umber, ivory, black.

10. Browns:

Acorn Brown. Sienna, carmine, Indian red, lampblack, ochre.

Brown. Indian red, lampblack, ochre.

Chocolate. Similar to acorn brown.

Cork Color. Base white, ochre, Indian red, lampblack, umber.

Dark Drab. Base white, Indian red, lampblack, Prussian blue, yellow ochre.

Doe Color. Base white, sienna, umber, ochre, lampblack.

Dove Color. Base white, Prussian blue, lampblack, ochre, Indian red, umber, sienna.

Drab. Base white, umber, Venetian red, yellow ochre, black.

Fawn. Base white, ochre, Indian red, lampblack, sienna, umber, chrome yellow, Venetian red.

Lava. Base white, black, chrome orange, chrome yellow.

Sandstone. Umber.

Snuff Brown. Base white, ochre, Indian red, Venetian red.

11. Greys and grays:[1]

Ash Gray. Base white, ochre, lampblack, sienna, ultramarine blue.

Dark Slate. Base white, Prussian blue, lampblack.

French Gray. Base white, black, ultramarine, Prussian blue, Venetian red.

Granite. Base white, ochre, lampblack.

Graystone. Base white, black, Prussian blue, ultramarine, Venetian red.

Lead. Base white, lampblack, Prussian blue.

Light Grey. Base white, lampblack, Prussian blue.

Pearl. Similar to French gray.

Silver Gray. Base white, ochre, lampblack, chrome yellow.

Smoke Gray. Base white, ochre, lampblack.

Steel Gray. Base white, chrome yellow, lampblack.

Stone Gray. Base white, chrome yellow, black.

Warm Gray. Base white, ochre, lampblack, sienna, Prussian blue.

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[1] Grey is understood to mean an admixture of black and white, while gray is an admixture of black and white to which another color has been added, provided, of course, that the black and white predominate.

CHAPTER II.

ANALYSIS OF THE VEHICLE.

12. Water, Occurrence. A fraction of 1 per cent of water may occur normally in the vehicle. A small percentage, 1 to 3 per cent, may be incorporated into the paint by the manufacturer under the belief that it secures better penetration when applied to surfaces that are slightly damp, and also that it will prevent the pigment from settling hard in the can. Oftentimes, however, large quantities are introduced for the purpose of cheapening the product. The water may be added to the paint and prevented from separating out, by forming an emulsion with the oil with the aid of an alkali, or by grinding it into the pigment, using an adhesive such as glue or casein. In the first case the nature of the ash left on burning some of the vehicle, separated as described under Linseed Oil, will indicate whether an alkali has been used or not. In the second case the vehicle will yield less than one per cent of water when distilled with a dry, inert substance such as sublimed lead, as the water remains with the pigment.

13. Detection. Water may be tested for qualitatively in light colored paints, by rubbing with a little eosin on a glass plate. If water is present the paint will take on a strong pink color, otherwise the color will remain practically unchanged. If the paint contains considerable coloring material, rendering the eosin test inapplicable, a weighed strip of gelatine may be immersed in the paint for several hours. If water is present the gelatine will soften and increase in weight, the adhering paint being removed by the use of petroleum ether and drying for a minute or two between sheets of filter paper. An immersion of the gelatine for 18 to 24 hours will show the presence of water in a paint containing as little as 2 per cent.

14. **Estimation.** Quantitatively, the water is best estimated by distillation, using a retort, the neck of which forms the inner tube of a condenser, the outside tube being a Welsbach chimney. One hundred grams of the paint is weighed into an aluminum beaker and mixed with a thoroughly dried, inert pigment like silica or sublimed lead until it ceases to be pasty, and then transferred to the retort, which is heated in an oil bath, the water being collected in a graduate calibrated to fifths of cubic centimetres. Toward the end of the distillation, the temperature of the contents of the retort being raised to 200° C., a very slow current of air or illuminating gas is admitted to the retort through a tube passing nearly to the surface of the pigment. This will carry over the last traces of moisture. It is advisable to pass the illuminating gas through a wash-bottle containing sulphuric acid, which not only serves to remove moisture, but acts as an indicator for the rate of flowing gas. The heating should be continued for at least two hours at the above temperature to insure the complete removal of the combined water from the basic carbonate of lead which may be present. This should be deducted from the total amount of water obtained, by multiplying the basic carbonate present by 2.3 per cent, which represents the average per cent of combined water in white lead. It is impossible to remove the water by this method, without decomposing part of the lead hydroxide of the white lead, as it begins to lose the combined water at 105°–120° C., the total

combined water being driven off at 150° C. for 6 hours with little or no loss of carbon dioxide. An exposure of 4 hours at a temperature 175° results in the loss of all

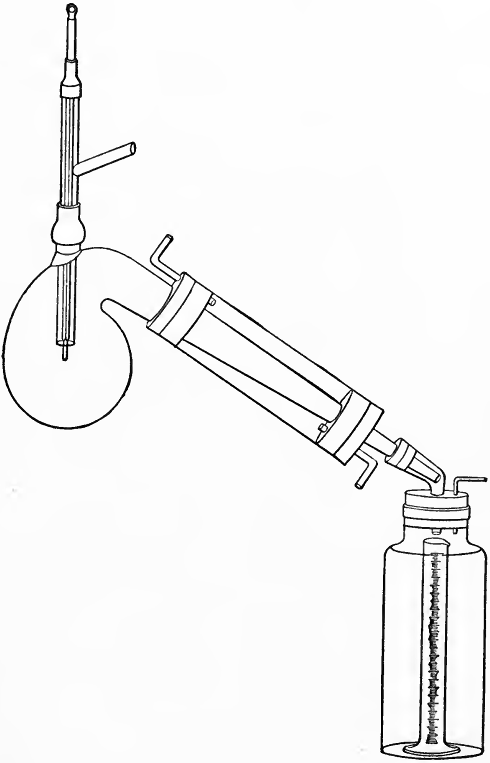

Fig. 3. — Estimation of Water.

the water and a slight amount of carbon dioxide; at 200° an exposure of 2 hours is sufficient to remove all of the combined water and about one-quarter to one-third of the carbon dioxide.

In each case a blank should be run in order to ascertain that the inert pigment and illuminating gas are free from condensible moisture.

The author believes that a current of air obtained by the use of an aspirator is preferable to the use of illuminating gas, as with the latter there is the possibility of the formation of water from the hydrogen of the illuminating gas and the lead oxide present, if the temperature is raised too high.

Of eighty mixed paints analyzed by the author, white and gray shades, the water content calculated on the basis of total vehicle, was as follows:

Amount of Water.	Number of Paints.
0 to 1 per cent	26
1 to 3 per cent	25
3 to 6 per cent	5
6 to 10 per cent	3
10 to 24 per cent	21

15. Linseed oil. *Extraction from paint.* One to two hundred grams of the paint are heated to about 65° C. on the water bath and centrifuged rapidly until the oil is freed from pigment. This operation may be conducted with advantage in a steam-heated Babcock milk tester.

16. Estimation of the volatile oils. The clear oil is weighed and introduced into a suitable sized Erlenmeyer flask connected with a rather large condenser. The contents of the flask are brought to 130° C. by means of an oil bath and a current of steam conducted through the oil. The volatile oils rapidly distil over and are collected in a weighed short-stemmed separatory funnel, the water being drawn off from time to time as may be necessary.

The distillate is allowed to stand for several hours to insure the complete separation of the water, which is then drawn off and the volatile oils weighed and bottled for subsequent examination. The aqueous portion of the distillate will inevitably carry with it a small quantity of volatile oil, but the amount will be slight, amounting to about 0.4 gram per 100 c.c. of water distillate. After calculating the percentage of volatile oil, the linseed oil is calculated by difference, by subtracting the percentages of volatile oil and water from 100.

The results obtained above may be checked up by weighing 6 or 7 grams of the thoroughly stirred paint into a weighed petri-dish and heating to 120° C. for 3 hours, cooling in a desiccator and weighing. A pure raw or boiled oil will undergo no appreciable change in weight, while the volatile matters will be practically all driven off. Knowing the amount of vehicle present, the percentage of the volatile oils may be readily calculated, and likewise the percentage of linseed oil.

The linseed oil, after being freed from the volatile oils, is allowed to stand for several hours in a warm place until thoroughly settled, and may then be tested for the presence of other oils as follows.

17. **Specific gravity.** Determine the specific gravity by means of a pycnometer or a Westphal balance.

The specific gravity may be taken at room temperature and calculated to 15.5° C.

Correction for 1° C. = .000650
Correction for 1° F. = .000361

The usual limits for pure raw oil at 15.5° C. are 0.931 to 0.937; boiled oils usually do not exceed 0.940. A low specific gravity may indicate:

a. Mineral oils.
b. Cotton-seed oil.
c. Corn oil.

A high specific gravity may indicate

a. Rosin or resinous products.
b. Rosin oils.
c. Excessive heating or unusual addition of metallic driers.

18. **Spot test.** One or 2 c.c. of the oil are poured on a porcelain plate and a drop of concentrated sulphuric acid added carefully. If pure, the spot formed will bear a marked resemblance to a begonia leaf. If rosin or rosin oil be present a black, gummy mass immediately results; cotton-seed oil gives a spot without the characteristic markings of the linseed-oil spot. Mineral oils give a scum-band rapidly spreading out over the surface from the drop, the margin of the band being uniformly circular. Fish oils give a similar reaction, but the margin of the band is not at all uniform, and may be readily distinguished from mineral oils. With a little practice and working with oils of known composition, this test can be relied upon to detect any appreciable adulteration with the above oils.

19. **Mineral oils.** The spot test for petroleum products may be confirmed by allowing a sample of the oil to flow down a sheet of glass, the other side of which has been painted jet black. If petroleum products are present even in a minute quantity, the sample will exhibit the "bloom" characteristic of mineral oils. A standard sample should always be run for comparison. It is possible to remove the "bloom" of mineral oils by the

use of nitrobenzine or similar compounds, but the author is of the belief that this is very seldom resorted to in the paint industry.

Quantitatively the mineral oil may be estimated by saponifying 10 grams of the oil with alcoholic potash for 2 hours, using a return condenser. The alcohol is distilled off and the soap dissolved in 75 to 100 c.c. of water, transferred to a separatory funnel and 50 c.c. of ether added. The liquids are then shaken, avoiding the formation of an emulsion as far as possible. The aqueous solution is then drawn off, the ethereal layer washed wtih a few cubic centimetres of water to which a little caustic potash has been added, and poured into a weighed flask. The soap solution is then returned to the separator, and twice extracted with ether in the same way as before. The combined ethereal solutions are distilled off on the water bath, the flask dried and weighed. The increase in weight represents the amount of unsaponifiable matter, and unless rosin oil is present, represents the mineral oil with the exception of about 2 per cent, the average amount of unsaponifiable matter in linseed oil.

20. The mineral oil may be separated from the rosin oil in the unsaponifiable material by heating 50 c.c. of nitric acid of 1.2 specific gravity to boiling in a flask of 700 c.c. capacity, the source of heat removed, and the unsaponifiable material added. The flask is then heated on the water bath with frequent shaking for about one-half hour, and 400 c.c. cold water added. After cooling, 50 c.c. of petroleum ether is added and the flask agitated, the mineral oil is dissolved, while the resinous matters remain in suspension. The liquid is then poured into a separatory funnel, leaving behind as much of the resinous material as possible. After settling, the aqueous liquid is drawn off and the ethereal layer poured into a weighed flask. Another portion of petroleum ether is added to the rosin remaining in the flask, and allowed to act upon it for about ten minutes, when it is added to that in the weighed flask. After distilling off the ether, the oil is weighed. Mineral oils lose about 10 per cent when treated with nitric acid in this way, and hence the weight of the oil found must be divided by 0.9 in order to find the amount present in the sample analyzed.

21. Cotton-seed oil. This oil is seldom found in house paints, but is often used in certain classes of barn paints. The spot test may be confirmed by the Halphen test, the apparatus required being a large test tube provided with a condensing tube and a brine bath; the reagent employed being a 1.5 per cent solution of sulphur dissolved in carbon bisulphide with an equal volume of amyl alcohol added. Equal volumes of the oil and reagent are heated in a steam bath at first, and after the violent boiling has ceased, in the brine bath at 105°–110° C. for about 30 minutes. As little as 1 per cent of cotton-seed oil will give a crimson wine coloration. Cotton-seed oil heated to 250° C. does not respond to this test.

Quantitatively, the amount of cotton-seed oil can only be approximated in a very general manner by means of the iodine values.

Let x = percentage of one oil, and
y = percentage of the other oil.
m = average iodine value of pure oil x.
n = average iodine value of pure oil y, and
I = iodine value of sample under examination.

Then

$$x = \frac{100\,(I - n)}{m - n}.$$

22. **Corn oil.** This oil gives a spot test much resembling that given by linseed oil, but may be detected in linseed oil, if in quantity, by the following test. Dilute with four volumes of benzine, add one volume of strong nitric acid, shake. Linseed oil turns a white color, while corn oil turns to a reddish orange.

Quantitatively, corn oil can be estimated only approximately when in linseed oil by the same method used for cotton-seed oil.

23. **Fish oils.** In addition to the spot test these oils may be detected by rubbing a little of the sample vigorously between the palms of the hands. Fish-oil mixtures give the characteristic odor of oils of this class.

In mixtures with linseed oil, the amount present can only be determined crudely by means of the " rise of temperature " with sulphuric acid with the Maumené apparatus described under the analysis of the Volatile Oils. Allen found the rise of temperature with sulphuric acid to be 104 to 111 in the case of linseed oil, and 126 in the case of menhaden oil.

24. **Rosin and rosin oils.** These products are best detected qualitatively by means of the Lieberman-Storch reaction, which is of sufficient delicacy to detect the presence of even very small quantities of rosin oil or rosin drier in boiled oil. One to 2 c.c. of the oil under examination are shaken in a test tube with acetic anhydride at a gentle heat, cool, pipette off the anhydride and place a few drops on a porcelain crucible-cover and add one drop of sulphuric acid (34.7 c.c. sulphuric acid and 35.7 c.c. water) so that it will mix slowly. If rosin or rosin oil is present, a characteristic, violet, fugitive color results. Certain fish oils will give a very similar color, but if present are easily detected by the fish-like odor of the oil on warming.

Old samples of pure boiled oil give a color that might be easily mistaken for rosin or rosin oils; in such cases it is best to warm the oil with alcohol so as to extract the bulk of rosin present and test the alcoholic extract. Rosin may be more completely separated and estimated by Twitchell's process (J. Soc. Chem. Ind., 1891, 10, 804) or by Gladding's method (Amer. Chem. J., 3, 416). This process depends upon the solubility of silver resinate in ether, while the silver salts of fatty acids are insoluble.

A much used test for determining the presence of a cheap rosin drier in boiled linseed oil, is to make a paste with the suspected oil and moisture-free litharge. If of good quality, the paste should not thicken or harden inside of 24 to 48 hours. If such hardening occurs, the oil should be condemned. A standard sample of oil should be run for comparison each time.

25. In the preparation of gloss paints a little varnish is added, the gums of which might be mistaken in the above tests for rosin. In the cheaper paints a large excess of rosin is used in the resinate drier added. An easy method of detecting rosin and other rosins and estimating the relative amount present, is to stir up about 100 grams of the paint with 500 c.c. petroleum ether, allow to stand 24 hours, siphon off the ether, and examine the skin formed on top of the pigment. This will harden in the course of another day so that it may be removed, placed on a watch glass, washed free of adhering pigment with more petroleum ether and dried. The color and other physical properties will enable one to judge whether it is rosin or some of the other varnish gums.

26. Linseed oil from inferior seed. This includes oil prepared from impure or adulterated seed, giving an oil of inferior quality; or, what is essentially the same thing, the screened foreign seeds are separately crushed and pressed and the resulting oil used to blend with a pure linseed oil. Such oils dry slowly and imperfectly, and the resulting film lacks the " hardness " given by the pure oils, and often give the consumer as just cause for complaint as the more grossly adulterated varieties.

When sold as raw oil, such oils usually have a greenish tinge which disappears or is masked in the boiling. Chemically this form of adulteration is more difficult to detect than when other oils of distinctively different chemical properties are used. With this class of oils, the specific gravity, iodine number, saponification value, and unsaponifiable matter remain nearly normal, and the leading tests that may be applied to such suspected oils are their oxygen absorption power and the time required for drying. Both the per cent of oxygen and the rate of absorption will be found markedly lower, depending on the amount of foreign seed oil present. In order to obtain comparable results, a standard oil of known purity should be carried through the tests along with the suspected oil, as the weather conditions may seriously affect the rate of drying.

27. Spread about one gram of precipitated lead, weighed off accurately, on a somewhat large watch glass in a thin layer, and then allow to fall on to it from a pipette 0.6 to 0.7 gram (not more) of the oil to be tested, placing each drop on a different portion of the lead, and taking care that the drops do not run into one another. Then allow the watch glass to stand at the ordinary temperature in a place exposed to light and protected from falling dust. Weigh at frequent intervals in order to note the rapidity with which the oil is absorbing oxygen and to determine accurately when the oil ceases to gain in weight. The lead powder is prepared by precipitating a lead salt with zinc, washing the precipitate rapidly in succession with water, alcohol and ether, and finally drying in a vacuum.

A weighed quantity of the oil will gain 16 to 17½ per cent in weight in drying; boiled oil somewhat less, varying from 15 to 17 per cent.

Instead of precipitated lead, thin aluminum plates 3 inches by 6 inches may be used. The plates are weighed, and 0.1 gram to 0.2 gram of oil rubbed over the plate, giving a thin uniform film, weighed, set aside in a dust-free place, and the increase in weight noted from time to time.

28. Specifications for boiled linseed oil, Navy Department, 1905. Must be absolutely pure kettle-boiled oil of the best quality, and the film left after flowing the oil over glass and allowing it to drain in a vertical position must dry free from tackiness in 12 hours at a temperature of 70° F.

It must contain no rosin. The specific gravity must be between 0.934 and 0.940 at 60° F.

To be purchased by the commercial gallon; to be inspected by weight, and the number of gallons to be determined at the rate of 7½ pounds of oil to the gallon.

CHAPTER III.

ANALYSIS OF THE VOLATILE OILS.

29. Identification. The volatile oil distilled from linseed oil is tested qualitatively for spirits of turpentine, stump turpentines, rosin spirit, petroleum naphtha and benzole by the following test.[1]

Shake in a test tube equal volumes of the turpentine to be tested and concentrated sulphurous acid until quite thoroughly mixed. Set aside, noting the time of separation and the color of the two strata. Samples of known purity should be run alongside of the sample to be tested, and the time of shaking the samples should be as uniform as possible. Deadwood turpentine if highly rectified gives a reaction approaching that of livewood turpentines.

1. *American Turpentine.*

Separation takes place *very slowly.*
Upper Stratum — Opaque; milky white.
Lower Stratum — Translucent; milky white.
Odor — Slight terpene smell.

2. *Russian Turpentine.*

Quick separation.
Upper Stratum — Translucent; faint turbidity.
Lower Stratum — Clear and colorless.
Odor — Slight pungent smell.

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[1] Scott's Test for Turpentines, Drugs, Oils and Paints, 1906.

3. *Deadwood Turpentine.*

Medium slow separation.
Upper Stratum — Opaque; light buff color.
Lower Stratum — Translucent; yellow-amber color.
Odor — Distinct tar smell.

4. *Livewood Turpentine.*

Medium quick separation.
Upper Stratum — Translucent; lemon yellow color.
Lower Stratum — Clear and colorless.
Odor — Mild tar smell.

5. *Rosin Spirit.*

Medium slow separation.
Upper Stratum — Translucent; golden-yellow color.
Lower Stratum — Translucent; creamy-white color.
Odor — Pungent rosin smell.

6. *Benzine (Petroleum Naphtha).*

Quick separation.
Upper Stratum — Clear and colorless.
Lower Stratum — Clear and colorless.
Odor — Sulphurous smell.

7. *Benzole.*

Quick separation.
Upper Stratum — Slight turbidity; faint yellow color.
Lower Stratum — Clear and colorless.
Odor — Benzole and sulphurous smell.

30. Estimation of petroleum products. If the qualitative test indicates the presence of live or dead wood turpentine in appreciable quantities, the amount of petroleum product that may be present is best estimated as follows:

A measured quantity of the volatile oil is allowed to drop slowly into 300 c.c. of fuming nitric acid, contained in a flask provided with a return condenser and immersed in cold water. A violent reaction takes place, and the flask should be shaken occasionally. When all action has ceased the contents of the flask is poured into a separatory funnel and thoroughly washed with successive portions of hot water to remove the products of the action of the acid on the turpentine. The remaining petroleum oil is separated and measured or weighed.

31. Wood turpentine being absent, the amount of petroleum products may be very closely approximated by the "Sulphuric Acid Number."

The apparatus and materials required being a large test tube of considerable diameter, bedded in closely packed cotton, in a fibre mailing case of suitable size, a thermometer provided with a platinum flange attached to the lower end, the lower part of the flange being bent at right angles to the stem of the thermometer. A mailing case packed with cotton offers considerable advantages over the regulation asbestos fibre mixed with plaster of Paris, in that if the test tube is broken during the estimation, the bottom of the mailing case may be readily removed and the acid soaked cotton replaced at once with fresh, while the plaster of Paris composition has to be washed and dried out, an operation requiring several hours.

32. A neutral mineral oil is required giving a rise when treated with sulphuric acid of not more than 3° C. Also a standard bottle of concentrated sulphuric acid kept for this purpose and a sample of turpentine known to be pure. Fifty c.c. of the neutral oil are pipetted into the large test tube, the temperature noted, and 20 c.c. of the acid, of the same temperature, added from the burette in a steady stream, stirring rapidly meanwhile with a uniform motion to maximum temperature, which is noted. After cleaning and cooling the apparatus, the experiment is repeated

exactly as before, but with the addition of 10 c.c. of pure turpentine to the neutral oil. The rise in temperature is again noted. Similar determinations are made with mixtures of 50 per cent of turpentine and 50 per cent benzine, and also of 75 per cent of turpentine and 25 per cent of benzine. Having thus ascertained standards for comparison, 10 c.c. of the sample under examination is carried through in exactly the same manner, the maximum temperature noted and the per cent of turpentine and of petroleum product calculated. Commercially pure turpentines will give closely uniform results; wood turpentines give lower figures which approach that of turpentine the more carefully the product is prepared and purified. Rosin spirits give a rise of 7° to 10° C., benzine and benzole 3° to 8° C.

Samples of turpentine which have been exposed to strong light are liable to have undergone oxidation changes which will markedly affect the " temperature rise." In which case, McIlhiney's bromine addition and substitution method will serve to distinguish such oxidized turpentines.

A scheme much in use by some paint chemists for separating mixtures of turpentine and benzine is to introduce 15 c.c. of the suspected sample into a glass-stoppered cylinder graduated to tenths of cubic centimetres, and then add 35 c.c. of cold concentrated sulphuric acid. Shake carefully 12 to 20 times, keeping the top of the cylinder turned away from operator. Allow to stand over night, and read off the volume of the benzine layer direct, the turpentine portion having combined with the sulphuric acid. There is considerable danger of an explosion in using this method; the danger, however, may be much reduced by cooling both the sample and acid to below 10° C.

33. ANALYSES OF VOLATILE OILS BY THE AUTHOR.

No.	Name of Oil.	Sp. Gr. at 22°C.	Odor.	Rise ° C.	Separation.	Lower Layer.	Upper Layer.
1	Terrabentine	.808	Petroleum	6°	Immediate	Clear	Slightly Milky
2	Turpentine	.855	Camphor Oil	52.5°	Rapid	Almost Clear	Lemon
3	Turpentine	.862	Characteristic Turpentine	57.0°	Medium	Slightly Milky	Milky
4	Off Color Turpentine	.857	"	30.5°	Slow	Clear	Clear
5	Turpentine	.853	"	48.3°	Slow	Milky	Milky
6	Turpentine	.860	"	56.7°	Medium	Milky	Slight tinge of Yellow
7	Wood Spirits Turpentine	.859	Stump Turpentine	52.8°	Slow	Deep Lemon	Milky
8	Turpalin Base	.862	Petroleum	1.0°	Quick	Clear	Clear

No. 1. Petroleum product, probably of Russian origin.
No. 2. Wood turpentine.
No. 3. Commercially pure turpentine.
No. 4. Spirits of turpentine containing about 50 per cent petroleum naphtha.
No. 5. Spirits of turpentine containing about 15 per cent petroleum naphtha.
No. 6. Poorly rectified turpentine.
No. 7. Stump turpentine.
No. 8. Petroleum product.

34. **Excessive use of volatile oils.** An excess of thinners or volatile oils is detrimental to the life of the paint. Sabin, in his work on "The Technology of Paint and Varnish," writes as follows:

"Most of the failures of lead and zinc paints are due to the use of these volatile thinners (turpentine and benzine). If raw linseed oil is used, it may be desirable to add 5 per cent of a good drier. This should be pale in color, indicating that it has been made at a low temperature, and should be free from rosin. The latter is not an easy thing to detect, but if a fair price is paid, say $1.50 to $2.00 a gallon at retail, and freedom from rosin is guaranteed by a maker of good reputation, the buyer ought to feel safe."

The presence of a large amount of thinners renders the paint easier to brush out, and hence the tendency has been to increase the amount of thinners, especially benzine because of its low cost, in mixed paints, resulting in the reducing of the linseed oil to a percentage below that required to give the proper life to the paint. The better class of paint manufacturers seem to consider 4 to 9 per cent of thinners sufficient for outside house paints.

Of 71 analyses of white and gray mixed paints made by the author, the amount of thinners came between the following limits:

Per cent Thinners.	Number of Paints.
0 to 4	6
4 " 5	5
5 " 6	1
6 " 7	6
7 " 8	10
8 " 9	5
9 " 10	11
10 " 11	4
11 " 12	2
12 " 29	21

Excluding the 21 paints containing 12 per cent of thinners and over, the average amount of thinners in the remaining 50 paints was 7.3 per cent. The paints high in thinners were, in almost every case, inferior paints, high in inert pigments.

CHAPTER IV.

SPECIAL METHODS ON OIL ANALYSIS.

35. Determination of the Iodine Number. The newer Hanus method for the estimation of the iodine number is to be preferred to the older standard Hubl method, as the Hubl solution rapidly loses strength on standing, is very slow in its reaction, and nearly every chemist using it employs a modification of his own, especially as regards the time for the solution to remain in contact with the fat or oil, and hence very different results may be obtained on the same oil or fat by different investigators. Comparative tests by the two methods made in this laboratory gave results which varied only a few tenths of one unit with oils of medium iodine values.

36. Preparation of Reagents. *Iodine Solution.* Dissolve 13.2 grams of iodine in 1000 c.c. glacial acetic acid (99.5 per cent acid, showing no reduction with bichromate and sulphuric acid); add enough bromine to double the halogen content determined by titration — 3 c.c. of bromine is about the proper amount. The iodine may be dissolved by the aid of heat, but the solution should be cold when bromine is added.

Decinormal sodium thiosulphate solution. Dissolve 24.8 grams of chemically pure sodium thiosulphate, freshly pulverized as finely as possible and dried between filter or blotting paper, and dilute with water to one litre at the temperature at which the titrations are to be made.

Starch paste. One gram of starch is boiled in 200 c.c. of distilled water for ten minutes and cooled to room temperature.

Solution of potassium iodide. One hundred and fifty grams of potassium iodide are dissolved in water and made up to one litre.

Decinormal potassium bichromate. Dissolve 4.9066 grams of chemically pure potassium bichromate in distilled water, and make the volume up to one litre at the temperature at which the titrations are to be made. The bichromate solution should be checked against pure iron.

37. **Determination.** *Standardizing the sodium thiosulphate solution.* Place 20 c.c. of the potassium bichromate solution, to which has been added 10 c.c. of the solution of potassium iodide, in a glass-stoppered flask. Add to this 5 c.c. of strong hydrochloric acid. Allow the solution of sodium thiosulphate to flow slowly into the flask until the yellow color has almost disappeared. Add a few drops to the starch paste, and with constant shaking continue to add the sodium thiosulphate until the blue color just disappears.

Weighing the sample. Weigh about 0.5 gram of fat or 0.250 gram of oil on a small watch glass or by other suitable means. With drying oils which have a very high absorbent power 0.100 to 0.200 gram should be taken. The fat is first melted, mixed thoroughly, poured on to the crystal and allowed to cool. Introduce the watch crystal into a wide mouth 16-oz. bottle with a ground-glass stopper.

Absorption of iodine. The fat or oil in the bottle is dissolved in 10 c.c. chloroform. After complete solution has taken place, 25 c.c. of the iodine solution are added. Allow to stand with occasional shaking for 45 minutes. The excess of iodine should be at least 60 per cent of the amount added.

Titration of the unabsorbed iodine. Add 10 c.c. of the potassium iodide solution and shake thoroughly, then add 100 c.c. of distilled water to the contents of the bottle.

Titrate the excess of iodine with the sodium thiosulphate solution, which is added gradually, with constant shaking, until the yellow color of the solution has almost disappeared. Add a few drops of starch paste and continue the titration until the blue color has entirely disappeared. Toward the end of the reaction stopper the bottle and shake violently, so that any iodine remaining in solution in the chloroform may be taken up by the potassium iodide solution.

Setting the value of the iodine solution. — At the time of adding the iodine solution to the fat, two bottles of the same size as those used for the determination should be employed for conducting the operation described above, but without the presence of any fat. In every other respect the performance of the blank experiments should be just as described. These blank experiments should be made each time the iodine solution is used. Great care must be taken that the temperature of the solution does not change during the time of the operation, as acetic acid has a very high coefficient of expansion, and a slight change of temperature makes an appreciable difference in the strength of the solution.

38. IODINE NUMBERS OF VARIOUS OILS.

Raw linseed oil	170–188
Boiled linseed oil	164–188
Bleached linseed oil	160
Chinese wood oil	163
Corn oil	111–123
Cotton-seed oil	101–117
Fish oil	148–160
Turpentine	331–368

39. Determination of the bromine absorption of oils, McIlheney's method.[1] The advantage of this method is,

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[1] J. Am. Chem. Soc. XXI, 1084.

that the absorption of halogen by addition is determined separately from the absorption by substitution, resulting in additional information as to the nature of the substance.

The process as at present used is as follows: A quantity of the oil to be analyzed is weighed into a glass-stoppered bottle, 10 c.c. of carbon tetrachloride added to dissolve the oil, and 20 c.c. of third-normal bromine in carbon tetrachloride added from a pipette. It is not found necessary in filling the pipette with bromine solution to use any special arrangement to prevent the introduction of bromine vapor into the mouth. Only a rubber tube is necessary. Another pipette full of solution should be added to 10 c.c. of carbon tetrachloride, and this blank titrated with thiosulphate to determine the strength of the bromine solution. The test itself need be allowed to stand only one or two minutes before adding 20 to 30 c.c. of 10 per cent solution of potassium iodide, the amount necessary depending upon the excess of bromine present. An excess, of course, does no harm. In order to prevent any loss of bromine or hydrobromic acid which would probably occur on removing the stopper of the bottle, a short piece of wide rubber tubing, of the sort used for Gooch crucibles, is slipped over the lip of the bottle so as to form a well around the stopper. It is advisable, also, to cool the bottle by setting it into cracked ice in order to produce a partial vacuum in the interior. Into the well formed by the rubber tubing is poured the solution of potassium iodide and the stopper opened slightly. If the bottle has been cooled with ice the iodide solution will be sucked into the bottle, and if it was not cooled some of the air from the interior of the bottle will bubble through the iodide solution, being thereby washed, and allow the iodide solution to enter the bottle. When sufficient iodide solution has been introduced the bottle is agitated to insure the absorption of the bromine and hydrobromic acid by the aqueous solution. The iodine now present is titrated with tenth-normal sodium thiosulphate, and when the titration is finished 5 c.c. of a neutral 2 per cent solution of potassium iodate are added. This liberates a quantity of iodine equivalent to the hydrobromic acid formed, and on titrating this iodine the bromine substitution figure may be calculated. The solution of potassium iodate should be tested for acidity by adding a measured quantity to a solution of potassium iodide, and if any iodine is liberated it should be determined with thiosulphate and a suitable correction introduced into the calculation. The potassium iodide, the thiosulphate solution, and the water used should all be tested to see that they are neutral.

The reaction between bromine and oil appears to be practically instantaneous as far as the bromine taken up by addition is concerned, but it seems likely that substitution is distinctly affected by the length of time that the oil and bromine are allowed to remain in contact.

40. Bromine values of various oils.

	No.	Hubl figure.	Bromine calculated from Hubl.	Per cent of bromine absorbed.	Bromine addition figure.	Bromine substitution figure.	Bromine from Hubl divided by bromine addition figures.
Raw linseed oil, several years old	1	166.9	105.2	98.4	95.4	1.5	1.103
Raw linseed oil, several years old	2	157.3	99.1	99.2	92.0	3.6	1.000
Raw linseed oil	3	184.2	116.1	116.1	109.6	3.4	1.059
Do.	4	178.6	112.6	108.5	102.1	3.2	1.102
Do.	5	185.9	117.2	113.2	109.2	2.0	1.072
Do.	6	186.3	117.0	112.2	106.5	2.9	1.098
Do.	7	...	...	104.5	99.9	2.3	...
Do.	8	...	...	115.1	109.5	2.8	...
Do.	9	...	...	114.6	109.4	2.6	...
Average omitting Nos. 1 and 2	...	183.8	115.7	112.0	106.6	2.7	1.083
Boiled linseed oil	1	180.4	113.7	106.0	100.8	2.6	1.126
Do.	2	183.3	115.5	110.8	105.8	2.5	1.091
Do.	3	...	...	105.4	101.2	2.1	...
Do.	4	...	...	110.0	103.2	3.4	...
Do.	5	...	...	109.8	105.2	2.3	...
Do.	6	...	...	113.6	103.0	5.3	...
Do.	7	...	...	109.2	103.8	2.7	...
Do.	8	...	...	110.8	101.0	4.9	...
Averages	...	...	...	109.5	103.0	3.2	...
Third run rosin oil	1	...	...	197.6	16.4	90.6	...
Do.	2	63.9	40.3	92.3	7.7	42.3	5.231
"Mystic" brand rosin oil	...	...	...	93.7	6.3	43.7	...
"Java" boiled rosin oil	...	73.3	46.2	101.9	8.3	46.8	5.685
Corn oil	1	...	...	76.2	73.8	1.2	...
Do.	2	...	...	75.8	73.2	1.3	...
Do.	3	...	...	75.4	71.6	1.9	...
Averages	...	...	...	75.8	72.9	1.5	...

41. Estimation of rosin in mixtures of linseed oil and mineral oil. Twitchell's method. A weighed portion of the sample is saponified by boiling with alcoholic potash; the alcohol is driven off by prolonged boiling after diluting with water. The unsaponifiable matter is shaken out with petroleum ether as previously described under Linseed Oil. The remaining soap solution made acid yielding a mixture of fatty and rosin acids. Heat until the fatty acids have separated on top. Cool, break the cake of fatty acids with a glass rod, pouring off the aqueous solution. Treat the acids again with boiling water, cool, remove to a porcelain dish, and dry at 100° C. until freed from all traces of water.

Two to three grams of the mixed fatty and rosin acids are weighed off accurately and dissolved in a flask in ten times their volume of *absolute alcohol*, and a current of dry hydrochloric acid gas passed through for about forty-five minutes or until the gas ceases to be absorbed. Allow to stand one hour, then dilute it with five times their volume of water and boiled until clear. From this point the analysis may be completed volumetrically or gravimetrically.

42. Volumetrically. The contents of the flask are transferred to a separatory funnel and the flask rinsed out several times with ether. After vigorous shaking the acid layer is run off and the remaining ethereal solution containing the rosin acids washed with water until the last trace of acid is removed. Fifty c.c. of alcohol are added and the solution titrated with standard caustic potash, using phenolphthalein as an indicator. The rosin acids combine at once with the alkali, whereas the ethylic esters remain unchanged. The number of c.c. of normal alkali used multiplied by 0.346 will give the amount of rosin in the sample.

43. Gravimetrically. The contents of the flask are mixed with a little petroleum ether, boiling below 80° C., and transferred to a separating funnel, the flask being washed out with the same solvent. The petroleum ether layer should measure about 50 c.c. After shaking, the acid solution is run off and the petroleum ether layer washed once with water, and then treated in the funnel with a solution of 0.5 gram of potassium hydroxide and 5 c.c. of alcohol in 50 c.c. of water. The ethylic esters dissolved in the petroleum ether will then be found to float on top, the rosin acids having been extracted by the dilute alkaline solution to form rosin soap. The soap solution is then run off, decomposed with hydrochloric acid, and the separated rosin acids collected as such, or preferably dissolved in ether and isolated after evaporating the ether. The residue, dried and weighed, gives the amount of rosin in the sample.

44. Determination of the free fatty acids in linseed oil. Ten grams of oil are weighed into a suitable sized Erlenmeyer flask and 50 c.c. of neutral, aldehyde-free alcohol added. The mixture is heated to about 60° C. for a minute or two, then cooled and titrated with tenth-normal alcoholic potash, using phenolphthalein as an indicator.

Oil made from mouldy seed, or seed contaminated with mustard oil, or oil containing rosin, will have a high acid figure. Pure raw oil should have a low acid figure, boiled oil will have a slightly higher figure.

Free mineral acid in bleached oil is determined by washing a definite weight of oil with water, separating the water, and titrating the dissolved mineral acid present.

Preparation of aldehyde, free alcohol for alcoholic potash solution. Dissolve 1.5 grams of silver nitrate in about 3 c.c. of water and add to a litre of alcohol in a glass-stoppered cylinder, mixing thoroughly. Dissolve 3 grams of pure potassium hydroxide in 10 to 15 c.c. of warm alcohol.

Cool, pour slowly into the alcoholic silver nitrate solution, without shaking. The silver oxide is precipitated in a finely divided condition. Allow to stand until the precipitate has completely settled. Siphon off the clear liquid and distil. The distillate will be neutral and free from aldehydes, and will not darken when used as a solvent for potash.

45. Determination of the saponification value. This value is also spoken of as the Koettstorfer number and Saponification number. In each case it is equivalent to the number of milligrams of potassium hydroxide necessary to saponify one gram of the oil.

Two grams of the oil are weighed out into a small Erlenmeyer flask and saponified with 25 c.c. of half-normal alcoholic potash, by heating gently on a water bath, a funnel being inserted in the flask. When the saponification is complete a few drops of phenolphthalein are added and the excess of alkali titrated with half-normal hydrochloric acid. A blank determination of the strength of the alcoholic potash should be made at the same time.

46. Determination of the flash point of linseed oil. For exact flash-point figures, rather expensive and complicated testers are needed; but for commercial tests that yield approximately the same figures, a very simple apparatus may be used, consisting of a two-ounce crucible, a thermometer reading at least 300° C., and a small gas jet attached to a rubber tube, a flame about the size of a pea being used. The cup is filled two-thirds full of oil, the bulb of the thermometer suspended in it, and the oil slowly heated. The determination should be carried on in a place entirely free from draughts. At short intervals the gas flame is brought close, but not touching, to the surface of the oil, with a slow, sweeping motion. The first distinct puff of pale blue flame that shoots across the surface of the oil indicates the flash point of the oil, and the temperature at which this occurs is noted.

47. Hurst states that linseed oil, whether raw or boiled, flashes about 243° C.; but these figures are considerably lower than those obtained in this laboratory, the raw oils flashing in the vicinity of 300° C., and the pure boiled oils from 275° to 300° C. Volatile oils used in the drier added to the oil, lower the flash point considerably, 4 or 5 per cent of volatile oil lowering the flash point to about 250° C. The other vegetable oils, as corn and cotton-seed oils, flash at nearly the same temperature as linseed oil. Mineral oils, such as would be used for adulteration, flash at 193° to 216° C., rosin oils at 140° to 167° C. The presence of rosin oil would also be indicated by the strong odor of rosin given off during the heating. Benzine and turpentine when present in linseed oil rapidly lower the flash point according to the percentage present, having a flash point themselves but little above that of room temperature.

48. Correction to be applied to the thermometer reading.

Let N = Length of exposed thread of mercury expressed in degrees.
T = observed boiling point.
t = temperature of the auxiliary thermometer, the bulb of which is midway between ends of the exposed mercury thread.
0.000154 = apparent coefficient of expansion of mercury in glass.
C = the correction in degrees.

Then $C = N\ (T - t) \times 0.000154.$

49. Evaporation test. This test will show very closely the amount of benzine added along with the drier in the preparation of boiled linseed oil.

Five grams of the oil to be tested are weighed into a small flat-bottomed evaporating dish and allowed to remain undisturbed at a temperature of 150° C. for three hours. The dish is then removed, cooled quickly, and immediately weighed. The loss in weight represents usually the greater portion of mineral oils, rosin oils or other volatile matters present in the sample.

J. Hortvet, state chemist for Minnesota, states that,

"Of fifteen samples represented as raw linseed oil, when subjected to this test, eleven showed no loss in weight, while four gave losses amounting to less than 0.3 per cent. Of one hundred and ten samples represented as boiled oils, sixty gave losses above 2 per cent, thirty-two showed no loss in weight, and of the remaining eighteen the loss was slight, seldom approaching 2 per cent. Forty-seven of the sixty samples which gave over 2 per cent loss were found to vary in specific gravity from 0.8835 to 0.9310. All samples not found adulterated by the usual tests showed a specific gravity of from 0.9310 to 0.9425, with the exception of one sample which had a specific gravity as low as 0.930, but by the other tests appeared to be straight raw linseed oil."

50. Determination of flash point and fire test of petroleum products, turpentine, etc. Covered testers. New York State Board of Health Tester. This instrument consists of a copper oil cup holding about 10 ounces heated in a water bath over a small flame. The cup is provided with a glass cover, holding a thermometer. This cover also has a hole for the insertion of the testing flame.

The test should be applied as follows:[1]

"Remove the oil cup and fill the water bath with cold water up to the mark on the inside. Replace the oil cup

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[1] Report New York State Board of Health, 1882, p. 495.

and pour in enough oil to fill it to within one-eighth of an inch of the flange joining the cup and the vapor-chamber above. Care must be taken that the oil does not flow over the flange. Remove all air bubbles with a piece of dry paper. Place the glass cover on the oil cup, and so adjust the thermometer that its bulb shall be just covered by the oil.

" If an alcohol lamp be employed for heating the water bath, the wick should be carefully trimmed and adjusted to a small flame. A small Bunsen burner may be used in place of the lamp. The rate of heating should be about two degrees per minute, and in no case exceed three degrees.

" As a flash torch, a small gas jet one-quarter of an inch in length, should be employed. When gas is not at hand employ a piece of waxed-linen twine. The flame in this case, however, should be small.

51. " When the temperature of the oil in the case of kerosene has reached 85° F., the testings should commence. To this end insert the torch into the opening in the cover, passing it in at such an angle as to well clear the cover, and to a distance about half-way between the oil and the cover. The motion should be steady and uniform, rapid, and without any pause. This should be repeated at every two degrees' rise of the thermometer, until the thermometer has reached 95°, when the lamp should be removed and the testings should be made for each degree of temperature until 100° is reached. After this the lamp may be replaced if necessary, and the testings continued for each two degrees.

" The appearance of a slight bluish flame shows that the flashing point has been reached.

" In every case note the temperature of the oil before introducing the torch. The flame of the torch must not come in contact with the oil.

"The water bath should be filled with cold water for each separate test, and the oil from a previous test carefully wiped from the oil cup."

52. **Open testers.** *Tagliabue's open tester.* This instrument is similar to the preceding, except that it is smaller, the oil cup being of glass and without a cover. The water bath is filled as before. The oil cup is filled to within three-thirty-seconds of an inch of the top. The heating flame is regulated to three-fourths of an inch in height, or at such height that the temperature of the oil is raised two and a half degrees per minute until 97° F. is reached, when the test flame is applied and the testings made every two degrees until the flash point is reached.

53. **Fire test.** The fire test is the temperature at which an oil will give off vapors, which when ignited will burn continuously. The cover is removed in the case of the closed tester, the heating being continued as described above. The flame may be extinguished by the use of a piece of asbestos board.

54. **Specifications for various oils.** It often devolves upon the paint chemist to examine various oils, some of which cannot be considered as paint oils, hence the following specifications adopted by the Treasury Department at Washington, 1907, of various oils will be of interest.

55. **Linseed oil.** It must be thoroughly strained and settled, transparent, free from suspended matter, and have the properties of a well-aged oil. The oil shall conform to the following physical and chemical tests: specific gravity at 15.5° C., not less than .933; flash point (open cup) not less than 280° C.; viscosity at 20° C., as determined by Engler viscosimeter (water being 100), not less than 750; iodine absorption number as determined by Wijs' method (time of absorption 2 hours), not less than 175; to be entirely free of all acids except fatty acids, of which not

more than 2 per cent calculated as linolic acid should be present; when heated to 300° C., and allowed to cool, the oil should show no suspended matter or deposit; and must show excellent drying qualities, as demonstrated by the Livache method.

56. **Deodorized benzine.** Should be a purified petroleum distillate, free from sulphur; specific gravity between .725 and .735 at 15.5° C.

57. **Engine oil.** Free running oil is required, consisting of 90 per cent refined petroleum, and 10 per cent pure acidless lard oil. The specific gravity should not be less than .905 at 15.5° C.; viscosity by Engler viscosimeter should not be less than 1550, and flash point less than 200° C. Samples that comply with the above requirements will be subjected to a practical test.

58. **High pressure cylinder oil.** An oil is required consisting of 90 per cent refined petroleum stock and 10 per cent of acidless tallow; specific gravity should not be less than .870 at 50° C.; flash point not less than 285° C.; viscosity by Engler viscosimeter should not be less than 2000 at 50° C., and not less than 350 at 97° C. The mixture should be neutral, free from adulterations, and suitable for use on engine cylinders with steam pressure of 125 pounds per square inch. Samples that comply with the above requirements will be subjected to a practical test.

59. **Lithographic varnish.** No. 0. Should be a varnish of the best quality of linseed oil and with a specific gravity of .940 at 25° C., and be suitable for making fine typographic inks.

No. 1. Requirements same as for No. 0, but with a specific gravity of .945 at 25° C.

No. 3. Requirements same as for No. 0, but with a specific gravity of .965 at 25° C.

60. **Kerosene oil.** Under this specification is required

refined petroleum, water white, specific gravity .790 to .810 at 15.5° C., and flash point not lower than 45° C.

61. **Lard oil.** Should contain the least possible quantity of free acid; should show a cold test of not over 4° C.; be free from adulterations, and have specific gravity of .914 to .916 at 15.5° C. The oil should be made from fresh lard, be free from admixture with other oils, and should respond to no test for cotton-seed oil.

62. **Sperm oil.** Should be pure winter-strained sperm oil, free from admixtures of any kind; specific gravity to be .875 to .884 at 15.5° C., and flash point 250° C.; viscosity as determined by Engler viscosimeter to be: at 20° C., not less than 495; at 50° C., not less than 220; and at 90° C., not less than 133.

63. **Gasoline.** Should be a refined petroleum product of .680 to .705 specific gravity at 15.5° C.

CHAPTER V.

ANALYSIS OF WHITE LEAD.

64. Color. The two samples are weighed out in gram lots on to a large glass plate, twelve drops of bleached linseed oil added to each and rubbed up thoroughly, and matched up on a microscope slide, the color being judged from both sides of the glass. After comparing the color, place the slide in the steam oven for two hours. This will give some idea as to the amount of yellowing that will occur when the lead is used in painting. This defect is particularly marked in pulp leads.

65. Lead acetate. The presence of lead acetate may be detected by pouring a few drops of a 10 per cent solution of potassium iodide upon the dry lead. If it turns yellow it contains acetate, while a well-washed sample will remain unchanged.

66. Opacity. Two grams each of the sample and standard are very carefully rubbed up with .01 gram of ultramarine blue and twenty-four drops of oil as described under the section on the Determination of the Tinting Strength of Colors. The more strongly the lead is colored, the weaker it is in hiding power or opacity. Adding weighed amounts of lead until the colors are of equal depth will show the ratio between the two.

67. Painting test. The painting value is best judged by painting test boards as described under the section on the Comparison of Paints for Covering Power, and afterwards exposing them under suitable conditions.

68. Sandy lead. One hundred grams of the paste lead are thinned with benzine and run through a fine bolting cloth, thoroughly stirred, and allowed to settle slightly for a short time only. The benzine portion is decanted and the sediment washed with benzine in a similar manner, until the benzine comes off nearly clear, leaving the sand alone as a residue. Sandy lead, while present in nearly all commercial lead, should be below 2½ per cent, but will sometimes be present in quantities as large as 10 per cent.

69. Foreign pigments. White lead is often adulterated with less expensive pigments, such as barytes (barium sulphate), zinc oxide, calcium carbonate, calcium sulphate, and the various kinds of silicates. On treating a small portion of the sample with acetic acid and diluting, the white lead and calcium salts will go into solution, leaving any lead sulphate, barytes, silica and silicates undissolved. Barytes is tested for by the flame test. Zinc is recognized by adding a few drops of potassium ferrocyanide to a portion of the clear acetic acid solution, a whitish precipitate of zinc ferrocyanide being obtained. Hydrogen sulphide is passed through the remainder of the acetic acid solution until all of the lead, and any zinc, are precipitated. Filter, and treat the filtrate with ammonium oxalate and leave in a warm place. A white precipitate indicates the presence of calcium compounds.

If the white lead is found to contain other pigments, the analysis is conducted as described under Analysis of White Paints.

70. Estimation of carbon dioxide. The amount of carbon dioxide in white lead may be estimated easily and accurately by means of Knorr's Apparatus or Scheibler's Apparatus.

KNORR'S APPARATUS.

(1) *Description of apparatus.* This apparatus (Fig. 4) employs only ground-glass joints, and may be quickly made ready for use or taken to pieces and packed away.

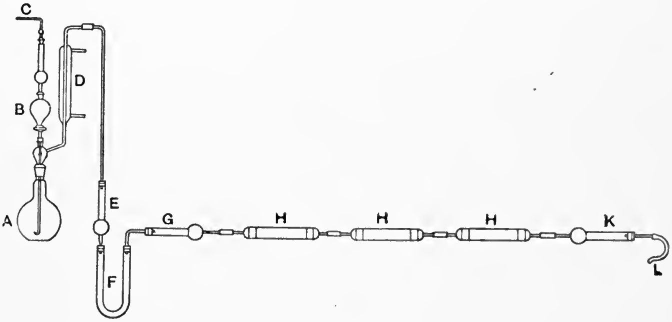

FIG. 4.—KNORR'S APPARATUS.

On the other hand, it is inflexible and must be carefully handled. *A* is distilling flask fitted to condenser by a ground-glass stopper; *B*, reservoir containing acid; *C*, soda-lime tube; *D*, condenser; *E*, calcium chloride tube; *F*, U-tube filled with pumice stone moistened with sulphuric acid, followed by a calcium-chloride tube *G*. The three soda-lime tubes *H*, *H*, *H* are followed by a calcium chloride tube *K*, which is connected with an aspirator at *L*.

The calcium chloride and soda lime employed should be finely granulated and freed from dust with a sieve.

71. One gram of the sample to be examined is placed in the distilling flask, which must be perfectly dry. The flask is closed with a stopper carrying the tube connecting with the absorption apparatus and also with the funnel tube. The tubes in which the carbon dioxide is to be absorbed are weighed and attached to the apparatus. In case two Liebig bulbs are employed, one for potassium hydroxide and the other for sulphuric acid, to absorb the moisture given up by the potassium hydroxide solution, it will be necessary to weigh them separately. If soda-lime tubes are employed it will be found advantageous to weigh them separately and fill the first tube anew when the second tube begins to increase in weight materially. The tube *B* is nearly filled with hydrochloric acid (sp. gr. 1.1), and the guard tube *C* placed in position. The aspirator is now started at such a rate that the air passes through the Liebig bulbs at the rate of about two bubbles per second. The stopper of the funnel tube is opened and the acid allowed to run slowly into the flask, care being taken that the evolution of the gas shall be so gradual as not to materially increase the current through the Liebig bulb. After the acid has all been introduced, the aspiration is continued, when the contents of the flask are gradually heated to boiling, the bulb in tube *B* being closed. While the flask is being heated the aspirator tube may be removed, although many analysts prefer when using ground-glass joints to aspirate during the entire operation. The boiling is continued for a few minutes after the water has begun to condense in *D*, when the flame is removed, the valve in the tube *B*, opened, and the apparatus allowed to cool with continued aspiration. The absorption tubes are then removed and weighed, the increase in weight being due to carbon dioxide.

72. **Scheibler's apparatus.** One-half gram of the sample is weighed into the flask *A* (see illustration), and 10 c.c. of dilute hydrochloric acid (sp. gr. 1.1) pipetted into the globe funnel *M*. A considerable number of glass beads should be added to the flask.

The stop-cock *G* is opened and the water in *F* forced up into the tubes *L* and *N* by pressing on the bulb *H*. Bring the water slightly above the zero mark at the top, and by opening the pinch-cock *O* bring the water in the tubes to a level on the zero mark.

The apparatus is now ready for the determination. Open the stop-cock *B* and allow the acid to flow slowly into the flask. The gas immediately begins to come off and pass into the rubber balloon *E*, which causes the water in *N* to be depressed and that in *L* to be correspondingly elevated. The pinch-cock *G* is opened and the water in *L* is allowed to flow out sufficiently fast to keep *L* and *N* as nearly on the same level as possible. When the water

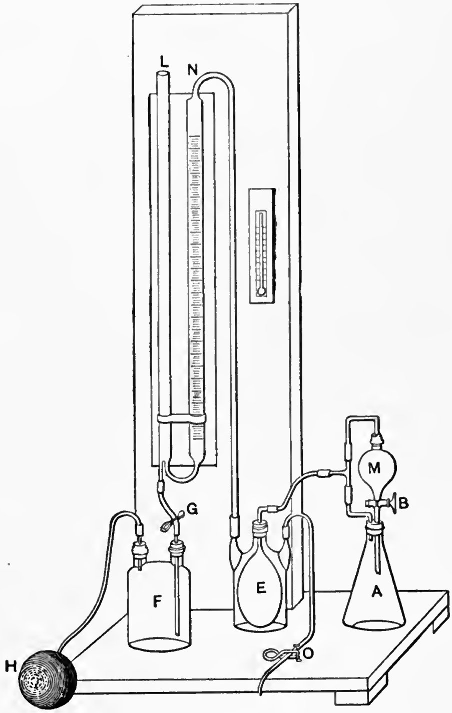

Fig. 5. — Scheibler's Apparatus.

ceases to be depressed in *N*, the pinch-cock *G* is closed and the apparatus allowed to stand five minutes, then the flask *A* is shaken three times at suitable intervals. At the end of half an hour all of the carbon dioxide should be expelled. The water in the tubes is brought to the same level and the burette reading made. A barometer reading should also be taken and the temperature of the thermometer on the instrument noted in order to correct for pressure and temperature. By referring to the following tables the per cent of carbon dioxide may be easily calculated.

EXAMPLE.

Weight of sample	0.5 gram.
Burette reading	30.3 c.c.
Barometer reading	750. m.m.
Thermometer reading	24° C.
Correction for absorption	5.09 c.c.
Gas evolved	30.30 c.c.
Total gas liberated	35.39 c.c.

Weight of 1 c.c. of carbon dioxide at 750 m.m. pressure and 24° C. = .001731 g.

$$35.39 \times .001731 = .06126 \text{ g.}$$

$$0.5 : 0.06126 :: 100 : x$$

x = 12.25 per cent carbon dioxide in sample.

NOTE. — In determining the amount of carbon dioxide in such products as "mineral primer" made from dolomitic limestone, the evolution of carbon dioxide is incomplete without boiling.

73. ABSORPTION OF CARBONIC ACID GAS, IN CUBIC CENTIMETRES OF CO_2, USING 10 C.C. OF DILUTE HYDROCHLORIC ACID (1.10 SP. GR.).

C. C. Evolved	1	2	3	4	5	6	7	8	9	10	C. C. Evolved
C. C. Absorbed	1.85	2.00	2.16	2.31	2.47	2.62	2.78	2.93	3.09	3.24	C. C. Absorbed
C. C. Evolved	11	12	13	14	15	16	17	18	19	20	C. C. Evolved
C. C. Absorbed	3.40	3.55	3.71	3.86	4.02	4.17	4.33	4.48	4.64	4.79	C. C. Absorbed
C. C. Evolved	21	22	23	24	25	26	27	28	29	30	C. C. Evolved
C. C. Absorbed	4.95	4.96	4.97	4.98	5.00	5.03	5.04	5.06	5.07	5.09	C. C. Absorbed
C. C. Evolved	31	32	33	34	35	36	37	38	39	40	C. C. Evolved
C. C. Absorbed	5.10	5.11	5.13	5.14	5.86	5.17	5.18	5.20	5.21	5.23	C. C. Absorbed
C. C. Evolved	41	42	43	44	45	46	47	48	49	50	C. C. Evolved
C. C. Absorbed	5.24	5.25	5.26	5.27	5.21	5.30	5.31	5.32	5.34	5.35	C. C. Absorbed
C. C. Evolved	51	52	53	54	55	56	57	58	59	60	C. C. Evolved
C. C. Absorbed	5.36	5.37	5.38	5.40	5.41	5.43	5.44	5.45	5.47	5.48	C. C. Absorbed
C. C. Evolved	61	62	63	64	65	66	67	68	69	70	C. C. Evolved
C. C. Absorbed	5.50	5.51	5.52	5.54	5.55	5.57	5.58	5.59	5.61	5.62	C. C. Absorbed
C. C. Evolved	71	72	73	74	75	76	77	78	79	80	C. C. Evolved
C. C. Absorbed	5.64	5.65	5.66	5.68	5.69	5.71	5.72	5.73	5.75	5.76	C. C. Absorbed
C. C. Evolved	81	82	83	84	85	86	87	88	89	90	C. C. Evolved
C. C. Absorbed	5.78	5.79	5.80	5.82	5.83	5.85	5.86	5.87	5.89	5.90	C. C. Absorbed
C. C. Evolved	91	92	93	94	95	96	97	98	99	100	C. C. Evolved
C. C. Absorbed	5.92	5.93	5.94	5.96	5.97	5.99	6.00	6.01	6.03	6.04	C. C. Absorbed

74. WEIGHT IN DECIMAL PARTS OF A GRAM OF ONE CUBIC CENTIMETRE OF CARBONIC ACID GAS (CO_2) DIETRICH TABLES.

C°.	720 m.m. 28.35 in.	722 m.m. 28.42 in.	724 m.m. 28.50 in.	726 m.m. 28.58 in.	728 m.m. 28.66 in.	730 m.m. 28.74 in.	732 m.m. 28.82 in.	734 m.m. 28.90 in.	736 m.m. 28.98 in.	738 m.m. 29.05 in.	740 m.m. 29.13 in.	742 m.m. 29.21 in.	744 m.m. 29.29 in.	746 m.m. 29.37 in.	C°.
10°	.001774	.001779	.001784	.001789	.001794	.001799	.001804	.001809	.001814	.001819	.001824	.001829	.001834	.001839	10°
11	.001767	.001772	.001777	.001782	.001786	.001791	.001796	.001801	.001806	.001811	.001816	.001821	.001826	.001831	11
12	.001759	.001764	.001769	.001774	.001779	.001783	.001788	.001793	.001798	.001803	.001808	.001813	.001818	.001823	12
13	.001751	.001756	.001761	.001766	.001771	.001776	.001780	.001785	.001790	.001795	.001800	.001805	.001810	.001815	13
14	.001743	.001748	.001753	.001758	.001763	.001768	.001773	.001777	.001782	.001787	.001792	.001797	.001802	.001807	14
15	.001735	.001740	.001745	.001750	.001755	.001759	.001764	.001769	.001774	.001779	.001784	.001789	.001794	.001799	15
16	.001727	.001732	.001737	.001742	.001746	.001751	.001756	.001761	.001766	.001771	.001776	.001781	.001786	.001791	16
17	.001719	.001724	.001729	.001733	.001738	.001743	.001748	.001753	.001758	.001763	.001767	.001772	.001777	.001782	17
18	.001711	.001715	.001720	.001725	.001730	.001735	.001740	.001745	.001749	.001754	.001759	.001764	.001769	.001774	18
19	.001702	.001707	.001712	.001717	.001722	.001727	.001731	.001736	.001741	.001746	.001751	.001756	.001760	.001765	19
20	.001694	.001699	.001704	.001708	.001713	.001718	.001723	.001728	.001733	.001737	.001742	.001747	.001752	.001757	20
21	.001686	.001690	.001695	.001700	.001705	.001710	.001714	.001719	.001724	.001729	.001734	.001739	.001743	.001748	21
22	.001677	.001682	.001687	.001691	.001696	.001701	.001706	.001711	.001715	.001720	.001725	.001730	.001735	.001739	22
23	.001669	.001673	.001678	.001683	.001688	.001692	.001697	.001702	.001707	.001712	.001716	.001721	.001726	.001731	23
24	.001660	.001665	.001669	.001674	.001679	.001684	.001688	.001693	.001698	.001703	.001707	.001712	.001717	.001722	24
25	.001651	.001656	.001661	.001665	.001670	.001675	.001679	.001684	.001689	.001694	.001698	.001703	.001708	.001713	25
26	.001642	.001647	.001652	.001656	.001661	.001666	.001670	.001675	.001680	.001685	.001689	.001694	.001699	.001704	26
27	.001633	.001638	.001643	.001647	.001652	.001657	.001661	.001666	.001671	.001676	.001680	.001685	.001690	.001695	27
28	.001624	.001629	.001634	.001638	.001643	.001648	.001652	.001657	.001662	.001667	.001671	.001676	.001681	.001686	28
29	.001615	.001620	.001625	.001629	.001634	.001639	.001643	.001648	.001653	.001658	.001662	.001667	.001672	001677	29
30	.001606	.001611	.001616	.001620	.001625	.001630	.001634	.001639	.001644	.001649	.001653	.001658	.001663	.001668	30

WEIGHT IN DECIMAL PARTS OF A GRAM OF ONE CUBIC CENTIMETRE OF CARBONIC ACID GAS (CO_2) DIETRICH TABLES.—Continued.

C°.	748 m.m. 29.45 in.	750 m.m. 29.53 in.	752 m.m. 29.61 in.	754 m.m. 29.68 in.	756 m.m. 29.76 in.	758 m.m. 29.84 in.	760 m.m. 29.92 in.	762 m.m. 30.00 in.	764 m.m. 30.08 in.	766 m.m. 30.16 in.	768 m.m. 30.24 in.	770 m.m. 30.32 in.	772 m.m. 30.40 in.	774 m.m. 30.48 in.	C°.
10°	.001844	.001849	.001854	.001859	.001864	.001869	.001874	.001879	.001884	.001889	.001894	.001899	.001904	.001909	10°
11	.001836	.001841	.001846	.001851	.001856	.001861	.001866	.001871	.001876	.001881	.001886	.001891	.001896	.001901	11
12	.001828	.001833	.001838	.001843	.001848	.001853	.001858	.001863	.001868	.001873	.001878	.001883	.001888	.001893	12
13	.001820	.001825	.001830	.001835	.001840	.001845	.001850	.001855	.001860	.001865	.001870	.001874	.001879	.001884	13
14	.001812	.001817	.001822	.001827	.001832	.001837	.001842	.001847	.001851	.001856	.001861	.001866	.001871	.001876	14
15	.001804	.001809	.001813	.001818	.001823	.001828	.001833	.001838	.001843	.001848	.001853	.001858	.001863	.001868	15
16	.001795	.001800	.001805	.001810	.001815	.001820	.001825	.001830	.001835	.001839	.001844	.001849	.001854	.001859	16
17	.001787	.001792	.001797	.001802	.001806	.001811	.001816	.001821	.001826	.001831	.001836	.001841	.001846	.001851	17
18	.001779	.001783	.001788	.001793	.001798	.001803	.001808	.001813	.001817	.001823	.001827	.001832	.001837	.001842	18
19	.001770	.001775	.001780	.001785	.001789	.001794	.001799	.001804	.001809	.001814	.001818	.001823	.001828	.001833	29
20	.001761	.001766	.001771	.001776	.001781	.001786	.001791	.001795	.001800	.001805	.001810	.001815	.001820	.001825	20
21	.001753	.001758	.001763	.001767	.001772	.001777	.001782	.001787	.001791	.001796	.001801	.001806	.001811	.001816	21
22	.001744	.001749	.001754	.001759	.001763	.001768	.001773	.001778	.001783	.001787	.001792	.001797	.001802	.001807	22
23	.001735	.001740	.001745	.001750	.001754	.001759	.001764	.001769	.001774	.001778	.001783	.001788	.001793	.001798	23
24	.001726	.001731	.001736	.001741	.001745	.001750	.001755	.001760	.001765	.001769	.001774	.001779	.001784	.001789	24
25	.001717	.001722	.001727	.001732	.001736	001741	.001746	.001751	.001755	.001760	.001765	.001770	.001775	.001780	25
26	.001708	.001713	.001718	.001723	.001727	.001732	.001737	.001742	.001746	.001751	.001756	.001761	.001766	.001771	26
27	.001699	.001704	.001709	.001714	.001718	.001723	.001728	.001733	.001737	.001742	.001747	.001752	.001557	.001762	27
28	.001690	.001695	.001700	.001705	.001709	.001714	.001719	.001724	.001728	.001733	.001738	.001743	.001748	.001753	28
29	.001681	.001686	.001691	.001696	.001700	.001705	.001710	.001715	.001719	.001724	.001729	.001734	.001739	.001744	29
30	.001672	.001677	.001682	.001687	.001691	.001696	.001701	.001706	.001710	.001715	.001720	.001725	.001730	.001735	30

75. ANALYSES OF WHITE LEADS BY AUTHOR.

No.	Sample.	Sandy Lead.	Carbon Dioxide.	Lead Hydroxide.	Lead Carbonate.
I.	Old Dutch Process White Lead . . .	6.25	11.35	31.11	68.89
II.	Old Dutch Process White Lead . . .	. . .	11.63	29.41	70.59
III.	Quick Corrosion White Lead	9.13	11.26	31.65	68.35
IV.	Kremnitz, White Lead	. . .	10.93	33.65	66.35

76. Determination of acetic acid in white lead. Thompson's method. Eighteen grams of the dry white lead are placed in a 500 c.c. flask, this flask being arranged for connection with a steam supply, and also with an ordinary Liebig condenser. To this white lead is added 40 c.c. of syrupy phosphoric acid, 18 grams of zinc dust, and about 50 c.c. of water. The flask containing the material is heated directly and distilled down to a small bulk. Then the steam is passed into the flask until it becomes about half full of condensed water, when the steam is shut off and the original flask heated directly and distilled down to the same small bulk — this operation being conducted twice. The distillate is then transferred to a special flask and 1 c.c. of syrupy phosphoric acid added to insure a slightly acid condition. The flask is then heated and distilled down to a small bulk, say 20 c.c. Steam is then passed through the flask until it contains about 200 c.c. of condensed water, when the steam is shut off and the flask heated directly.

77. These operations of direct distillation and steam distillation are conducted until 10 c.c. of the distillate require but a drop of $\frac{N}{10}$ alkali to produce a change in the presence of phenolphthalein. Then the bulk of the distillate is titrated with $\frac{N}{10}$ sodium hydroxide, and the acetic acid calculated. It will be found very convenient in this titration, which amounts in some cases to 600–700 c.c., to titrate the distillate when it reaches 200 c.c., and so continue titrating every 200 c.c. as it distils over.

If the dry white lead under examination has been obtained by extraction as a residue from white lead paste, it is well that this extraction should be exceedingly thorough, as, otherwise, fatty acids may be held and distilled with the acetic acid. Even then they will not interfere with the final titration, as they may be filtered from the distillate before titration, should that be desired.

78. ANALYSES OF MISCELLANEOUS WHITE LEADS MADE BY THE AUTHOR.

No.	Net Weight.	White Lead.	Lead Sulphate.	Zinc Oxide.	Barytes	Calcium Carbonate.	Silica.	Clay.	Undetermined.
I.	13.5 oz.	9.98	...	12.00	76.28	...	1.10	...	0.64
II.	15.4 oz.	64.73	...	3.60	30.43	...	0.76	...	0.48
III.	14.8 oz.	4.69	...	12.50	75.72	5.89	0.67	...	0.53
IV.	15.0 oz.	3.34	...	8.96	72.35	4.52	...	10.83	...
V.	...	54.69	...	17.38	25.57	...	...	...	0.36
VI.	1 lb. 14.2 oz.	...	3.29	6.90	89.81	...	...	...	...
VII.	1 lb. 14 oz.	10.69	...	20.03	69.28	... ...	...	...	...
VIII.	15 oz.	5.31	6.37	13.68	74.25	...	...	...	0.39

None of the above products are entitled to be called white lead. Only one bore the name of the company putting out the product.

79. Short weights of white lead packages. All the white leads and so-called white leads, examined by the writer, have been found to be short weight. That is, the kegs supposed to contain 12½ pounds will actually contain in each eight kegs, which should have shown 100 pounds, only 83 to 89 pounds. As showing to what extent the different so-called white leads actually varied and fell short in weight, I give the following list.

Number.	Assumed Weight.	Net Weight.	
	Lbs.	Lbs.	Oz.
I	50	46	0
II	12½	11	13
III	12½	10	6
IV	12½	10	7
V	25	21	12
VI	25	22	7
VII	12½	10	0
VIII	12½	11	0

CHAPTER VI.

ANALYSIS OF SUBLIMED LEAD, ZINC OXIDES AND ZINC-LEAD PIGMENTS.

Analysis of Sublimed Lead.[1]

80. Lead and zinc oxide. Weigh one gram into a small beaker, add 20 c.c. of 10 per cent sulphuric acid, stir well and allow to stand 10 minutes, filter, wash slightly with dilute sulphuric acid on filter.

Residue. Dissolve through filter with hot, slightly acid ammonium acetate solution, wash with hot water, dilute to 200 c.c. with hot water. Add slight excess of potassium bichromate solution and heat. Filter on Gooch crucible, wash with water. Dry, ignite and weigh as lead chromate.

Filtrate. Add about 2 grams of ammonium chloride, heat to boiling, add excess of ammonia and filter. Reject residue. Add 1 gram of microcosmic salt and a very slight excess of acetic acid. Boil, cool, filter on Gooch crucible, and wash with water. Ignite and weigh as zinc pyrophosphate. Calculate to zinc oxide.

81. Sulphates. Dissolve 0.5 gram in water 25 c.c., ammonia 10 c.c., hydrochloric acid in slight excess.

Dilute to 200 c.c. and add a piece of aluminum foil which should about cover the bottom of the beaker. It is important that this be held at the bottom by a glass rod. Boil gently until the lead is precipitated. Completion of this is shown by the lead ceasing to coat or cling to the alumi-

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[1] The author is indebted to L. S. Hughes of the Picher Sublimed Lead Company for this method.

num. Decant through a filter, pressing the lead sponge into a cake to free it from solution. Add to filtrate a little sulphur-free bromine water, boil and precipitate as barium sulphate in the usual manner.

82. Sulphur dioxide. Treat two grams with 5 per cent sulphuric acid and tritrate with $\frac{N}{100}$ iodine. A quick method of calculating the lead sulphate and oxide from the above data is the following: Multiply the weight of barium sulphate from one gram by 1.3, which gives the weight of lead sulphate. Multiply the same weight of barium sulphate by 0.888 and deduct this result from the total lead found. Multiply the difference by 1.077, which will give the lead oxide.

83. Composition of sublimed lead. The approximate composition of sublimed lead as stated by the manufacturers is as follows: —

	Per cent.
Lead sulphate	75
Lead oxide	20
Zinc oxide	5
	100

the lead sulphate and lead oxide being apparently combined as a white oxysulphate. The zinc oxide is incidental to the manufacture.

ANALYSES OF SUBLIMED LEAD BY THE AUTHOR.

	I. Per cent.	II. Per cent.
Lead sulphate	75.02	80.29
Lead oxide	18.48	14.46
Zinc oxide	6.22	5.18
Silica, alumina, and ferric oxide	0.28	.07
	100.00	100.00

The Identification and Estimation of Sublimed White Lead in Mixtures.[1]

84. Neutral ammonium chloride solution will dissolve the lead compounds of sublimed white lead; also the hydrate of corroded white lead, zinc oxide, and some calcium sulphate. It leaves undissolved calcium carbonate, zinc sulphide, normal lead carbonate, and the content of lead carbonate in corroded lead.

To determine the sublimed white lead in a pigment containing the above ingredients, boil the sample with a considerable excess of strong neutral ammonium chloride solution, filter hot on the pump, and wash with hot dilute neutral ammonium chloride.

85. The lead, zinc, lime and sulphuric anhydride are determined in the filtrate. The required sulphur trioxide is combined with the lime, and the rest with the lead. Any excess of lead is contingent in its application upon the amount of lead found undissolved by the ammonium chloride.

If there is an appreciable amount of this residual carbonate, the required hydrate is calculated, and a deduction made from the excess lead found in the filtrate. Any lead in the original filtrate not satisfied is now calculated to lead oxide and regarded as the lead oxide of sublimed white lead, and the lead sulphate and zinc oxide thereof calculated and deducted from the total of these compounds.

It will be noted that the conditions above considered are much more complex than need be anticipated in the analysis of actual paints.

Extraction of lead sulphate by the above treatment prevents the necessity of considering the sulphuric anhy-

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[1] The author is indebted to L. S. Hughes for this method.

dride of possible barium sulphate, and leaves the original residue in such shape that if it contains both the carbonate and sulphate of barium they can be conveniently separated.

Analysis of Zinc Oxides, Leaded Zincs, and Zinc-Lead Whites.

86. Moisture. Heat 2 grams at 105° C. for 3 hours, cool and weigh.

87. Sulphur dioxide. Weigh 2 grams into a 250 c.c. beaker, add 100 c.c. of distilled water that has been *freshly boiled* and cooled, and 5 c.c. of concentrated sulphuric acid; allow to stand 15 minutes. Titrate with standard hundredth normal iodine solution, using starch paste as an indicator.

1 c.c. hundredth normal iodine = .001269 grams iodine.

Wt. iodine × 0.252 = wt. sulphur dioxide.

The presence of sulphur dioxide in appreciable amounts in zinc oxide pigments should be considered highly undesirable, as it tends to cause the manufactured paint to harden in the package.

Preparation of reagents. Iodine solution. Dissolve 12.685 grams of pure iodine and about 18 grams of potassium iodide in about 150 c.c. of water in a graduated litre flask. After solution, fill to the mark with water that has been freshly boiled.

Sodium thiosulphate. Dissolve 25 grams in a litre of water that has been freshly boiled.

Starch paste. One gram of starch is boiled in 200 c.c. of distilled water.

Standardizing the sodium thiosulphate solution. Place 20 c.c. of standard potassium bichromate solution in a glass-stoppered flask, add 10 c.c. of a 15 per cent solution of potassium iodide. Add to this 5 c.c. of strong hydrochloric acid. Allow the solution of sodium thiosulphate to flow slowly into the flask until the yellow color has almost disappeared. Add a few drops of starch paste, and with constant shaking, continue to add the sodium thiosulphate until the blue color just disappears.

88. Zinc sulphate. Zinc oxide not being soluble in less than one million parts of water, according to Comey, any zinc sulphate present may be dissolved out. Weigh 5 grams on to a filter, add 20 c.c. of hot water, repeat with two more additions. Titrate the hot filtrate with ferrocyanide of potash after making acid with acetic acid. Calculate soluble zinc to zinc sulphate. The zinc oxide should not be subjected to a prolonged boiling, owing to possible interaction between the lead sulphate and zinc oxide.

89. Insoluble matter. Dissolve 1 gram in 20 c.c. of strong hydrochloric acid, add 50 c.c. of water, boil 10 minutes more. Filter, wash with boiling hot water, ignite, and weigh. Unless the sample is adulterated, the insoluble matter is usually reported as silica.

90. Lead. To filtrate from 89, add 3 c.c. of concentrated sulphuric acid, stir and evaporate until white fumes of sulphur trioxide appear. Cool, add 30 c.c. water to dissolve the zinc sulphate, warm, add 50 c.c. alcohol, allow to stand one-half hour, filter on Gooch crucible, washing first with water containing 2 per cent of sulphuric acid, finish washing with 50 per cent alcohol. Dry, ignite over ordinary lamp for two or three minutes, at low red heat, and weigh as lead sulphate.

91. Sulphuric acid. Dissolve 0.5 gram of pigment in

Water 25 c.c.
Ammonia 10 c.c.
Hydrochloric acid in slight excess.

Dilute to 200 c.c. and add a piece of aluminum foil, which should about cover the bottom of the beaker. It is important that this be held at the bottom by a glass rod. Boil gently until the lead is precipitated. Completion of this is shown by the lead ceasing to coat or cling to the aluminum. Decant through a filter, pressing the lead sponge into a cake to free it from solution. Add to filtrate a little sulphur-free bromine water, boil to expel bromine, add 15 c.c. of barium chloride, boil 10 minutes, filter, wash with hot water, ignite and weigh as barium sulphate, calculate to sulphur trioxide by multiplying by 0.3433.

92. **Zinc oxide.** To the filtrate from 90, which contains the zinc, evaporate excess of alcohol, add sodium carbonate in excess, boil, settle, decant several times on to filter, in order to remove the sodium salts, and finally wash thoroughly with hot water. Dry, and remove precipitate as free as possible from filter paper. Ignite filter in a weighed porcelain crucible and cool. Add the precipitate, ignite gently at first, and then at red heat to constant weight, weigh as zinc oxide. If desired the zinc may be estimated volumetrically, as described under the analysis of white paints.

93. **Calculations.** Deduct the sulphuric acid combined with the zinc as zinc sulphate from the total combined sulphuric acid. Calculate the remainder to lead sulphate by multiplying the combined sulphuric acid (sulphur trioxide) by 3.78. Deduct the calculated lead sulphate from the total lead which was weighed as sulphate, and calculate the remaining lead to lead oxide by multiplying the lead sulphate by 0.7359. Calculate the zinc sulphate to zinc oxide by multiplying by 0.503, and deduct from total zinc oxide. The difference is the zinc oxide in the sample.

94. **Classification.** For convenience the American zincs may be divided into the following classes:

1. *Green seal* and *Florence red zinc oxides*, which are similar to the imported zinc oxides, being made by the sublimation of the metal itself, and hence constitute the purest types of zincs.

2. *New Jersey zinc oxides*, made directly from the Franklinite ore. These zinc oxides, while not as white as those sublimed from metallic zinc, are very pure, usually running over 99 per cent zinc oxide. The following analyses[1] are representative of this class of zincs:

	I.	II.
Moisture	0.03	0.06
Silica, etc.	0.08	0.19
Zinc sulphate	0.11	0.15
Lead sulphate	0.03	.02
Zinc oxide	99.75	99.58
	100.00	100.00

3. *Mineral Point zincs*, manufactured at Mineral Point, Wisconsin; these contain a varying amount of lead sulphate and usually appreciable amounts of zinc sulphate as shown in the following analyses.[1]

	I.	II.
Sulphur dioxide	...	trace
Lead sulphate	4.22	5.98
Zinc sulphate	1.41	0.61
Silica	0.06	0.05
Zinc oxide	94.31	93.36
	100.00	100.00

4. *Leaded zincs*, made in Missouri and Kansas, which contain a much larger percentage of lead sulphate than the Mineral Point zincs.

ANALYSES OF LEADED ZINCS BY THE AUTHOR.

	I.	II.	III.
Moisture	0.03	0.02	0.04
Sulphur dioxide	0.30	0.29	0.50
Zinc sulphate	0.86	1.49	1.26
Lead sulphate	26.46	19.76	23.06
Zinc oxide	72.11	78.11	74.72
Undetermined	0.24	0.33	0.42
	100.00	100.00	100.00

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[1] Analyses made by the author.

5. *Zinc-lead white*, prepared mostly from Colorado zinc-lead ores, which also usually carry copper, silver, and gold. The prepared pigment has a specific gravity of about 5.5, and consists mainly of zinc oxide and lead sulphate in about equal portions. In color it is not as white as pure zinc oxide. In some cases, at least, arsenic compounds are present in considerable amounts. Samples examined by the author had the following compositions.

	I.	II.	III.	IV.
Moisture	0.29	0.58	0.20	0.26
Sulphur dioxide	0.01	0.01	0.01	0.01
[1] Arsenious oxide	0.68	0.47	0.32	1.60
[1] Antimony oxide	0.20	0.33	0.20	0.88
Silica	0.14	...	0.05	0.04
Zinc sulphate	0.78	0.55	1.61	0.84
Lead sulphate	46.00	48.80	46.66	49.82
Zinc oxide	51.70	49.15	50.90	46.48
Undetermined	0.20	0.11	0.05	0.07
	100.00	100.00	100.00	100.00

Sulphur dioxide, whether occluded, combined, or both, is considered the most objectionable constituent of zinc pigments, and many chemists reject shipments containing more than 0.06 per cent sulphur dioxide. Zinc sulphate ranks next as an objectionable constituent, although the percentage permitted is considerably higher. Pigments containing over one per cent of zinc sulphate are considered undesirable, and are usually rejected.

95. Estimation of arsenic and antimony in zinc-lead whites.[2] Weigh 2 grams of the sample into a 200 c.c. digestion flask. Add 7 grams of potassium bisulphate, 0.5 gram of tartaric acid, and 10 c.c. of concentrated sulphuric acid. Digest carefully at first, but finally with the full power of a Bunsen burner, until a clear mass remains, containing but little free sulphuric acid. Cool,

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[1] Owing to the conditions of production it is assumed that the arsenic and antimony exist in the forms represented.

[2] This method is essentially that of A. H. Low, Chemical Engineer, Vol. 5, No. 3, page 125.

spreading the melt around on the sides of the flask. Add 50 c.c. of water, 10 c.c. of strong hydrochloric acid, and digest for about 20 minutes without boiling. Cool thoroughly under the tap, and filter off the separated lead sulphate. Dilute the filtrate to about 300 c.c. with hot water, maintain the liquid warm, and pass in hydrogen sulphide for about 15 minutes or until precipitation is complete. Filter, washing with hydrogen sulphide water. Digest filter and contents in a rather small amount of yellow ammonium sulphide. Filter on suction cone, washing with as small a quantity of water as possible.

96. Digest the filtrate with 3 grams of potassium bisulphate and 10 c.c. of strong sulphuric acid, over a free flame until all of the free sulphur and the larger portion of free acid is expelled. Cool, spreading the melt around on the sides of the flask as before. Add 25 c.c. of water and 10 c.c. of strong hydrochloric acid, and warm to effect complete solution. Cool under the tap, add 40 c.c. of strong hydrochloric acid, and pass in hydrogen sulphide until complete precipitation of the arsenic takes place, 15–30 minutes. The antimony remains in solution. Filter off the precipitated arsenious sulphide on to a weighed Gooch crucible, washing with a mixture of two volumes of hydrochloric acid and one of water. The filtrate is reserved at this point for the estimation of antimony. The precipitate is next washed with alcohol, the crucible and contents placed in a small beaker, the crucible nearly filled with carbon bisulphide, and the contents allowed to digest at ordinary temperature for about 20 minutes in order to dissolve the free sulphur. The carbon bisulphide is removed by suction, the crucible dried in the steam oven, cooled, and the precipitate weighed as arsenious sulphide and calculated to arsenious oxide.

Wt. arsenious sulphide × 0.8043 = wt. arsenious oxide.

97. Instead of weighing as the sulphide, the arsenic may be estimated volumetrically as follows: Wash out the hydrochloric acid from the sulphide precipitate with hydrogen sulphide water. Digest filter and contents in a little warm ammonium sulphide, filter on a suction cone, washing with a little dilute ammonium sulphide solution. Place the filtrate in digestion flask, add 2 to 3 grams of potassium bisulphate and 5 c.c. of strong sulphuric acid. Evaporate, boiling to a small bulk, and then manipulate the flask over a free flame until the sulphur is entirely expelled and most of the free acid also. Take up, after cooling, by warming with 50 c.c. of water, and then boil sufficiently to expel any possible sulphur dioxide. Now drop in a bit of litmus paper as an indicator, and then add ammonia until the solution is slightly alkaline. Again slightly acidify with hydrochloric acid and cool to room temperature. Finally, add 3 to 4 grams of sodium acid carbonate and a little starch, liquor and titrate with standard iodine solution. Pay no attention to a slight discoloration toward the end, but proceed slowly until a single drop of the iodine produces a strong permanent blue color.

The iodine solution may be prepared by dissolving about 11 grams of iodine in a little water with the addition of about 20 grams of potassium iodide and diluting to 1 litre. Standardize with arsenious oxide. Dissolve about 0.150 gram in 5 c.c. of strong hydrochloric acid by warming very gently, dilute and neutralize as described above, and finally titrate with the iodine solution. One c.c. of the latter will equal about 0.003 gram of arsenic.

98. Antimony. Very nearly neutralize the filtrate, reserved for the antimony estimation with hydrochloric acid, dilute with double its volume of hot water, and pass in hydrogen sulphide until all of the antimony is precipitated. Filter washing with hydrogen sulphide water.

Digest filter and contents in a little ammonium sulphide, filter on suction cone and wash with dilute ammonium sulphide. Place the filtrate in the digestion flask and add about 3 to 4 grams of (pure) potassium bisulphate and 10 c.c. of strong sulphuric acid. Boil as previously described to expel, first the water, then all the free sulphur, and finally most of the free acid. Cool, add 50 c.c. of water and 10 c.c. of strong hydrochloric acid. Heat to effect solution, and then boil for a few minutes to expel any possible sulphur dioxide. Finally, add 10 c.c. more of strong hydrochloric acid, cool under the tap, dilute to about 200 c.c. with cold water and titrate with a standard solution of potassium permanganate. The solution ordinarily used for iron titrations will answer. The oxalic acid value of the permanganate multiplied by 0.9532 will give the antimony value.

CHAPTER VII.

ANALYSIS OF ZINC SULPHIDE WHITES AND INERT PIGMENTS.

Analysis of Lithopone, Ponolith, Etc.

99. **Moisture.** Heat 2 grams at 105° C. for 3 hours. Loss in weight represents hygroscopic moisture.

100. **Barium sulphate.** To 1 gram add 10 cc. of hydrochloric acid and 10 c.c. of water, heat gently until excess of acid has been expelled, dilute with 100 c.c. of water, and boil gently for 10 minutes. Filter, ignite and weigh residue as barium sulphate.

101. **Total zinc.** Neutralize the filtrate from the barium sulphate with ammonia, make distinctly acid with hydrochloric acid, heat to about 80° C. and titrate with standard potassium ferrocyanide as described under Analysis of White Paints.

102. **Zinc sulphide.** Fuse 1 gram in a large crucible with a mixture of potassium nitrate and potassium chlorate for about half an hour. Dissolve the fused mass in dilute hydrochloric acid, and boil the solution with strong nitric acid for half an hour. Filter off the insoluble residue, precipitate the combined sulphuric acid in the filtrate with barium chloride in the usual manner, filter, ignite, and weigh.

Wt. barium sulphate $\times$ 0.1373 = wt. sulphur.

Calculate sulphur to zinc sulphide.

103. **Zinc oxide.** Calculate excess of zinc over what is required to form the zinc sulphide to zinc oxide.

104. **Calcium.** Occasionally zinc sulphide whites are found on the market, in which the barium sulphate has

been wholly or partially replaced with calcium sulphate, in which case the calcium is estimated in the usual manner, after the removal of the zinc as sulphide, and the sulphuric acid combined with the calcium determined as usual. The sulphuric acid due to the calcium must be deducted from the total sulphuric acid obtained by oxidation before calculating to zinc sulphide.

If desired, the total sulphur may be determined by treating 1 gram of the pigment with dilute hydrochloric acid, potassium chlorate in small quantities, and sufficient bromine to insure complete oxidation. Soluble combined sulphuric acid may be determined by pouring *boiling* dilute hydrochloric acid on a weighed portion of the pigment, filtering, and precipitating with barium chloride as usual.

105. ANALYSES OF ZINC SULPHIDE WHITES BY AUTHOR.

	I. Lithopone.	II. Ponolith.
Moisture	0.20	0.18
Barium sulphate	69.62	69.19
Zinc sulphide	28.05	28.07
Zinc oxide	1.55	2.27
Undetermined	0.58	0.29
	100.00	100.00

Analysis of White Mineral Primer, White Ochre, Magnesite, Whiting, Paris White, English Cliffstone, Etc.

106. Moisture. Heat 2 grams at 105° C. for two hours, cool and weigh.

107. Silica. Weigh one-half gram into a suitable sized casserole. Cover, add 5 c.c. of hydrochloric acid (sp. gr. 1.1) by means of a pipette, without raising the cover. After the effervescence has ceased, rinse off the beaker cover with a little hot water. Evaporate to dryness and cool. Add 2 c.c. of concentrated hydrochloric acid, again evaporate, and heat gently for a few minutes. Cool, and dissolve up in 100 c.c. of hot water and 10 c.c. of strong hydrochloric acid, filter, wash, ignite, and weigh. If 1 per cent or under, it may be regarded as silica. If more, it should be fused with sodium carbonate, dissolved up in water and hydrochloric acid, in the same casserole, and evaporated to dryness. Heat gently. Add a little more hydrochloric acid and dehydrate again. Finally, take up in water acidulated with hydrochloric acid, filter, ignite and weigh as silica. The filtrate from the silica fusion is treated as described under 111.

108. Alumina and iron. The filtrate from the original residue is made just perceptibly alkaline with dilute ammonia, the iron and alumina filtered off, ignited and weighed in the usual manner.

109. Calcium. The filtrate from the iron and alumina is made acid with acetic acid, boiled, and 40 c.c. to 50 c.c. of ammonium oxalate solution added. Continue boiling for 5 minutes, filter, and wash thoroughly. Return filter and precipitate to same beaker. Add 200 c.c. of boiling water and 25 c.c. of dilute sulphuric acid and titrate with standard tenth-normal potassium permanganate.

1 c.c. tenth-normal permanganate = 0.0028 g. CaO
1 c.c. tenth-normal permanganate = 0.0050 g. $CaCo_3$
1 c.c. tenth-normal permanganate = 0.0086 g. $CaSO_4.2H_2O$
1 c.c. tenth-normal permanganate = 0.0068 g. $CaSO_4$
1 c.c. tenth-normal oxalic acid = 0.0028 CaO
Cryst. oxalic acid × 0.444 = CaO

Example: Wt. sample taken = 0.250 g.
Titration with permanganate = 50.5 c.c.
25 c.c. standard iron solution = 31.8 c.c. permanganate
1 c.c. standard iron solution = .007 g. iron, or .01 g. Fe_2O_3.
1 c.c. tenth-normal iron solution = .0056 g. iron
25 c.c. standard iron solution = 31.25 c.c. tenth normal permanganate.
1 c.c. permanganate solution used = 0.983 c.c. tenth-normal permanganate.
50.5 c.c. × 0.983 = 4964 c.c.
(49.64 c.c. × 0.0050) ÷ 0.250 = 99.28 % $CaCoO_3$.

110. **Magnesium.** The filtrate from the calcium oxalate is cooled and treated with hydrogen sodium phosphate, allowed to stand for one-half hour, 25 c.c. of strong ammonia added, allowed to stand one hour, filtered on a Gooch crucible, ignited and weighed.

Wt. precipitate × 0.7575 = wt. magnesium carbonate.

111. **Calcium and magnesium oxides.** The filtrate from the silica fusion should be treated separately from the main filtrate, as the calcium and magnesium obtained from it are to be reported as oxides and not as carbonates. Precipitate the iron and alumina, calcium and magnesium as described under 108, 109, and 110.

112. *Note.* If the sample contains considerable magnesium carbonate, the following modification should be observed. After filtering off the iron and aluminium hydroxides, they are redissolved in another beaker, diluted, and again precipitated and filtered into the main filtrate. The same treatment is given to the calcium oxalate. Magnesium compounds when present in considerable percentages badly contaminate the other precipitates.

113. ANALYSES OF CALCIUM AND MAGNESIUM CARBONATE PIGMENTS BY AUTHOR.

	I. White Ochre.	II. Whiting.	III. English Cliffstone.	IV. Magnesite.
Moisture	0.11	0.30	1.60	0.07
Silica	1.21	0.90	2.02	2.04
Iron oxide and alumina	.63	0.20	1.00	3.01
Calcium carbonate	97.39	96.55	92.81	10.84
Magnesium carbonate	0.56	1.84	2.52	83.91
Undetermined	0.10	0.21	0.05	0.13
	100.00	100.00	100.00	100.00

114. *Analysis of Agalite, Terra Alba, Etc.* These pigments have essentially the same composition — calcium sulphate plus 2 molecules of water. The same method of

analysis may be pursued as described under the analysis of calcium carbonate pigments. In addition, it is necessary to determine the combined water by ignition to constant weight, and also to determine the combined sulphuric acid, which may be done as follows:

Boil 0.5 gram of the pigment in 30 c.c. of strong hydrochloric acid for 10 minutes in a covered beaker. Dilute with 250 c.c. of boiling water, boil 5 minutes, filter, make filtrate neutral with ammonia, then distinctly acid with hydrochloric acid, and bring to boiling. Add 25 c.c. of barium chloride, boil 10 minutes, filter, wash with hot water, ignite and weigh.

Wt. barium sulphate × 0.3433 = combined sulphuric acid.

115. ANALYSES OF CALCIUM SULPHATE PIGMENTS BY AUTHOR.

	I. Agalite.	II. Terra Alba.
Moisture and combined water	19.02	20.67
Iron oxide and alumina	0.29	0.67
Silica	5.60	0.70
Calcium sulphate	74.90	76.52
Magnesium sulphate	...	1.36
Undetermined	0.19	.08
	100.00	100.00

Analysis of Silicas, Clays, and other Insoluble Silicates.

116. The silicas used in the manufacture of paints and especially in wood fillers are obtained either by pulverizing quartz, which is practically pure silica, or from natural deposits where it occurs in a finely divided form usually containing other minerals.

China clay is a natural product, being essentially a hydrated silicate of alumina. Its composition varies according to the locality from which it is obtained.

117. Fusion with sodium carbonate. One-half gram is thoroughly mixed with 10 grams sodium carbonate and one-half gram potassium nitrate placed in a covered platinum crucible and fused until quite clear and quiet. Cool, and dissolve in water in a casserole, provided with beaker cover, on the hot plate. Make acid with hydrochloric acid, adding the acid with a pipette, keeping the casserole covered to avoid loss. Also rinse out the crucible with a little acid. After the effervescence is over, wash off the watch glass, and evaporate to dryness on the sand bath. Cool, moisten residue with hydrochloric acid and evaporate to complete dryness again. Dissolve in 10 c.c. of hot water and 10 c.c. of hydrochloric acid. Filter, ignite and weigh precipitate as silica.

If barytes is suspected to be present, the sodium carbonate fusion is dissolved in hot water and the barium carbonate filtered off, dissolved in hydrochloric acid, and precipitated with a few drops of sulphuric acid in the usual manner. The filtrate from the barium sulphate is added cautiously to the filtrate from the barium carbonate, the mixed filtrate made acid and the silica dehydrated as described above.

118. The filtrate from the silica is made slightly alkaline with ammonia, and the iron and alumina precipitated, washed, redissolved, reprecipitated to free from sodium salts, filtered, ignited and weighed in the usual manner.

The filtrate from the iron and alumina is treated with ammonium oxalate, and after being allowed to stand in a warm place the calcium is filtered off, ignited and weighed as calcium oxide. If desired the calcium may be estimated volumetrically, as described under the analysis of white mineral primers, etc.

The filtrate from the calcium is tested for magnesium with sodium hydrogen phosphate and if found, estimated in the usual manner.

The carbon dioxide is determined in a separate portion of the sample. The amount found is combined with the requisite amount of calcium to form calcium carbonate. Any excess of calcium is reported as the oxide, it being in combination with the silica. The magnesium is usually calculated as magnesium oxide unless the carbon dioxide is in excess of the calcium present, in which case it is calculated to magnesium carbonate and the remainder of the magnesium to the oxide.

119. **Moisture.** Heat 2 grams at 105° C. for 3 hours, cool and weigh.

120. **Combined water.** Weigh 2 grams into a platinum crucible, heat in the muffle or over a strong Bunsen flame for 1 hour. Loss in weight equals combined water unless an appreciable amount of carbonate is present.

121. **Determination of the alkali metals, sodium and potassium.** Heat gently 1 gram of the sample intimately mixed with 1 part ammonium chloride to 8 parts of pure calcium carbonate. The alkalies as well as some of the calcium are converted into chlorides. Cool, treat with water. The alkali chlorides will dissolve, while most of the calcium remains undissolved. Filter, precipitate the calcium with ammonia and ammonium carbonate filter, evaporate to small bulk, and precipitate any remaining calcium. Filter. The solution now contains as fixed compounds only sodium and potassium chlorides. Evaporate nearly to dryness in a weighed platinum dish on water bath. Cover and dry completely on the hot plate, exercising great care to prevent the spattering of the material. Finally heat gently with a Bunsen burner, which must be held in the hand and the flame waved under the dish and removed as soon as any portion of the dish becomes red hot. Cool and weigh. Take up in water and add an excess of platino-chloride solution. Evaporate to a syrupy

consistency, take up with 80 per cent alcohol, filter on to a weighed Gooch crucible, and wash with alcohol. Dry in the steam oven.

Wt. of precipitate × 0.1941 = wt. potassium oxide.

Calculate to potassium chloride, subtract from the weight of the mixed chlorides, thus obtaining the weight of sodium chloride which may then be calculated to sodium oxide.

122. ANALYSES OF SILICAS BY AUTHOR.

	I.	II.	III.
Moisture	0.21	0.06	0.43
Ferric oxide and alumina	0.28	0.01	1.48
Silica	99.40	99.88	53.48
Calcium carbonate	...	...	26.12
Magnesium carbonate	...	...	18.17
Undetermined	0.11	0.05	0.32
	100.00	100.00	100.00

ANALYSES OF MAGNESIUM SILICATES BY AUTHOR.

	I.	II.
Moisture	0.50	0.29
Combined water	2.99	3.44
Silica	58.60	56.76
Ferric oxide	0.09	0.18
Alumina	1.43	2.84
Calcium carbonate	...	2.77
Calcium oxide	5.63	...
Magnesium oxide	30.45	33.50
Undetermined	0.31	0.22
	100.00	100.00

ANALYSIS OF TOLANITE BY AUTHOR.

Moisture	0.22
Combined water	10.42
Ferric oxide	0.09
Alumina sol. in HCl	0.39
Silica	65.51
Alumina	23.12
Undetermined	0.25
	100.00

TYPICAL ANALYSES OF CLAYS.[1]

	I.	II.	III.	IV.
Silica	45.45	66.20	72.66	64.84
Alumina	38.75	24.11	17.33	24.31
Ferric oxide	1.15	0.79	1.05	1.60
Calcium oxide	...	...	0.13	0.11
Magnesium oxide	0.11	...	...	...
Potassium oxide	0.17	0.96	0.36	0.24
Sodium oxide	...	...	0.38	0.32
Combined water, etc.	13.05	7.20	8.09	8.58
Undetermined	1.32	0.74	...	...
	100.00	100.00	100.00	100.00

123. Specifications for paste wood filler. (*Bureau of Supplies and Accounts, Navy Department*, 1902.) Paste wood filler shall contain the following:

	Per cent.
Silicate	65
Raw linseed oil	10
Best quality rubbing varnish	25

The silicate must be dry, finely ground, and when subjected to microscopic test the particles must show a needle-pointed shape. Powdered silicate which shows spherical fragments will not be accepted.

The raw linseed oil must be absolutely pure, well-settled oil, of the best quality; must be perfectly clear, and not show a loss of over 2 per cent when heated to 212° F., or show any deposit of foots after being heated to that temperature. The specific gravity must be between 0.932 and 0.957 at 60° F.

The rubbing varnish to be of the very best quality, and to be equal in quality to the standards of rubbing varnish, which can be seen on application to the general storekeeper's office at the various navy yards. Any indication of the use of rosin or any other adulterant in this varnish will be sufficient for its rejection.

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[1] Geological Survey of N. D., 1901.

The paste wood filler when thinned with turpentine to a brushing consistency must dry hard on glass in 24 hours. It must not rub up by friction under the finger, and when immersed in water must remain intact for at least 4 hours. It must dry full without lustre, and transparent, so that it will not color or cloud the work, and hard enough to stand sandpaper without clogging the paper after 12 hours.

CHAPTER VIII.

DETERMINATION OF FINENESS, COVERING POWER AND TINTING STRENGTH OF PIGMENTS.

124. Determination of the comparative fineness of pigments. The comparative fineness, or perhaps better, the rate of settling of pigments, may be determined by means of the following apparatus.

A is an ordinary graduated cylinder holding 100 c.c.

B is a black metal shield attached to the block *D*, which half surrounds the cylinder, and is provided with a round opening $\frac{3}{16}$ of an inch in diameter, exactly opposite the 25 c.c. graduation.

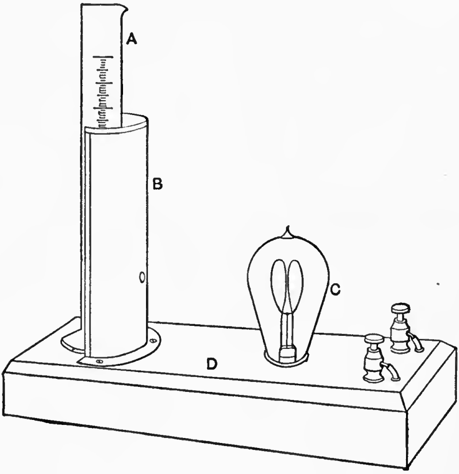

FIG. 6.

C is an electric light.

The cylinder is filled to the one hundred c.c. mark with

87° gasoline; 2 grams of the pigment to be tested are introduced, the cylinder stoppered, shaken 25 times with a uniform motion and the stop watch started with the last shake. The cylinder is placed in position and the time noted until the outlines of the aperture can be plainly observed. This gives an excellent method of determining the comparative fineness of pigments of the same type.

125. Comparison of paints for covering power. The following method described by G. W. Thompson, though open to criticism, furnishes in many cases much valuable data.

"Use white pine boards, 30 inches long by 10 inches wide, and, approximately, 1 inch thick. Each end of the board is provided with a cleat having a tongue fitting into a groove on the end of the board and securely nailed on. The entire board, including the cleats, to be finished to the size given above. Three of these boards may be primed with, say, the following paint mixture:

White lead paste	100 lbs.
Linseed oil, — $\frac{1}{3}$ boiled	75 lbs.

No attempt is made to secure a definite amount of priming paint to the unit of surface; this, for the reason that the boards may vary considerably in their absorptive power. When this priming coat is dry, each board receives a diagonal stripe of lampblack in japan about 1 inch wide on one or both sides of the board, as may be desired. When this black stripe is dry it is given a second coat of paint mixed to a consistency proper for painting, the formula being recorded.

126. "The weight per gallon of the paint so mixed is then obtained by finding its specific gravity and multiplying by 8.33, which gives the weight per gallon. Inasmuch as the board used has a total surface of 680 square inches, all that is required to do is to find what the ratio is between 680 square inches and the spreading rate at which it is desired to apply the paint in order to find the fraction of the gallon to be applied to each board. If the rate adopted is 1200 square feet to the gallon, then we get the formula:

$$680 \text{ sq. inches} : 1200 \text{ sq. feet} :: 1 \;.\;.\; x,$$

the reciprocal of 'x' being the fraction of a gallon of paint to be applied to each board, one coat. Having the weight of the paint per gallon we easily get the amount of paint by weight to apply to each board, one coat on all sides. When this second coat of paint is thoroughly dry, a similar coat is applied; and, when dry, the boards can be compared for the covering power of the paints on them. We mention the painting of three boards with each paint to be compared. The purpose of this is that variations in results are obtained between boards which are apparently painted in an identical manner. These variations are not great, but it is thought best to eliminate them, to a certain extent, by painting three boards and selecting the one giving medium results for comparison with boards painted with other paints."

127. Determination of the tinting strength of colors. The determination of the tinting strength of color pigments is a very necessary operation in the valuation and use of color pigments. The colors should always be compared with a carefully selected standard.

128. Chrome yellows, ochres and greens. Weigh out .05 gram of color, place on a large glass plate, add 12 drops of bleached linseed oil, and rub up with a flat-bottomed glass pestle or muller, then add 1 gram of zinc oxide, kept solely for this purpose, and grind with a circular motion fifty times, gather up with a sharp-edged spatula and grind out twice more in like manner, giving the pestle a uniform pressure.

Weigh out .05 gram of the color kept as the standard, and treat in exactly the same manner as described above. Transfer the standard to a microscope slide and spread out evenly, drawing the spatula in one direction only, and that toward the end of the slide. In like manner transfer the prepared sample to the slide, spread out evenly as before, drawing the spatula in the same direction as directed above, and bringing the edge of sample carefully to the edge of the standard. Compare the tints as shown on both sides of the glass.

129. **Reds, red oxides, etc.** Use 0.02 gram of sample to one gram of zinc oxide.

130. **Blues and blacks.** Use 0.01 gram of sample to 2 grams of zinc oxide with 24 drops of oil.

131. **Paste goods.** For testing the strength of paste goods a can containing pure zinc oxide ground in bleached linseed oil should be kept on hand.

132. **Chrome yellows, ochres and greens.** Use 0.5 gram of sample to 10 grams of zinc paste. Weigh accurately on balanced glasses and grind as described above.

133. **Reds, red oxides, etc.** Use 0.2 gram of sample to 10 grams of zinc oxide paste.

134. **Blues and blacks.** Use 0.05 gram sample to 10 grams of zinc oxide paste.

135. GRAVITY AND VOLUME OF PIGMENTS.[1]

Name of Pigment.	Sp. Gr.	Volume loose Pigment wt. per gal. in lbs.
White lead, Dutch Process	6.750	15.17
Sublimed lead	6.396	11.18
Zinc lead	5.635	6.64
Lead sulphate	6.082	9.77
Zinc oxide Green Seal	5.470	3.57
Zinc oxide, selected	5.554	6.36
Lithopone	4.236	8.80
Barytes, domestic	4.482	16.96
Barytes, blanc fixe	4.329	12.95
Eng. C. S. Paris white	2.705	6.85
Precipitated chalk	2.580	2.82
Terra Alba, French	2.358	6.74
Silica, floated	2.596	6.47
Silica, ground	2.550	4.40
English china clay	2.596	3.83
Talc	2.749	6.72
Chrome yellow, light	6.413	6.12
Chrome yellow, medium	5.842	6.57
Chrome yellow, deep	5.910	12.06
Litharge, yellow	8.663	32.21
Litharge, red	8.781	24.07
Rochelle ochre	2.802	5.61
Red lead, English	8.681	26.22
Tuscan red, dark	3.660	12.76
Chrome green, light	5.754	11.51
Chrome green, medium	5.239	13.05
Prussian blue	1.956	2.83
Chinese blue	1.903	3.85
German ivory black	2.619	4.55
Frankfort black	2.935	6.17
Bone black	2.319	5.19
Graphite	2.293	8.69

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[1] Drugs, Oils and Paints, Vol. XXI., page 299.

CHAPTER IX.

THE PRACTICAL TESTING OUT OF PAINTS.

136. **Paints should be tested out by the chemist.** The chemical analysis of a can of paint will tell much regarding the value of that paint, but a thorough practical testing out on a suitable surface will tell more, and the two in conjunction should render the chemist's report complete and above question. Often, however, the testing out is done by a so-called " practical man " who has little or no knowledge of chemistry, and his report for that very reason is apt to be misleading to the chemist. In order to secure the most desirable results, the chemist should do his own testing out, and this involves a practical painting knowledge that can be gained only by experience and under the guidance of an able master painter.

137. **Equipment.** The chemist, if he is to do his own testing out, should provide himself with an ample equipment so that he may carry on his work unhampered. He should have mixing cans large enough to hold sufficient paint for the coat to be applied and to allow stirring without danger of slopping over the side. A number of flat paddles of suitable sizes, a set of measures and a strainer, are also essential articles. All paint from the priming to the finishing coat should be strained, as it assists in securing a more uniform mixture than can be obtained by stirring. This is especially necessary where tints are to be tried out.

138. The chemist should be provided with a good set of brushes. It is a serious mistake to work with too few

brushes. For ordinary testing, the author believes that oval brushes should be used, and never a large flat brush which simply mops the paint on and does not assist it in penetrating into the fibres of the wood. An oval brush, being necessarily stiffer, rubs the oil and pigment into the wood, thoroughly satisfying it. For trimming and finishing the edges, a good chiselled varnish brush can be used with advantage. Having provided himself with a good set of brushes, the paint chemist should take good care of them. New brushes should never be placed in water. At the close of the day's work, they may be laid out full of paint on a board, but should not be left this way for more than twenty-four hours. When through with the brushes for a time, they should be laid in a regular paint trough, containing raw oil, or they may be suspended in a can of raw oil containing a little turpentine, to prevent the oil from becoming fatty. They should not be allowed to stand on end, as it turns the painting edge of the brush. Neither should brushes be allowed to remain for long intervals in cans of paint. Brushes should never be allowed to get " lousy " through the paint drying on the bristles. In use, the brush should be handled in such a manner as to wear the bristles to a chisel edge-like point, and should never be jabbed into corners, but carefully worked in.

139. **The requisites for a paint.** The requisites for a high-grade paint are:

a. Covering power,
b. Spreading capacity,
c. Durability,
d. Wearing evenly,
e. Failing by gradual wear, and
f. Leaving a good surface for repainting.

In order to test out a paint to determine to what degree it will fulfil the above requirements, the chemist must have a clear understanding of the practical application of paint and the suitability of different surfaces to receive paint of varying consistencies.

140. Relation of the surface to the paint. The surface on which the paint is to be tested out is of prime importance, as it vitally affects the oil and turpentine reduction which should be given the paint. If the surface is a dense close-grained wood, a much more liberal turpentine reduction must be used than when the surface is more porous, as in the case of soft pine. The lumber used should be well seasoned and entirely free from dampness; and for outside paints, the surface should be exposed to the direct rays of the sun for at least a couple of days before applying the paint, even if the surface is apparently free from moisture. If the test is to be applied on a new building, every precaution should be taken that the lumber has dried out thoroughly after the plastering has been done. It must be remembered that there are eighty to ninety gallons of water in every hundred square yards of plaster, and if the house is kept closed during the time the plaster is drying, the moisture must pass through the clapboard siding, over which the paint is to be spread, in order to escape. This operation is much slower and takes a great deal longer time for completion, than most paint men believe. This is especially true if the house is sheathed with one or more thicknesses of paper, between the boarding and siding. If the tests are to be placed on small test-frames, such as are described below, or on specially constructed test fences, the conditions affecting the application of the paint can be more easily controlled.

141. Test structures. A convenient, practical, and efficient method of conducting exposure tests is shown in the illustration at the beginning of this book, which represents the first of a series of tests which are being conducted by the North Dakota Government Experiment Station.

This structure is 75 feet in length, 6 feet 6 inches high, begins 15 inches from the ground, and faces east and west. The posts are 5 feet apart and bedded in concrete. One side of the structure is plain boarded, the other side clapboarded, the top capped, and the ends boxed in a suitable manner. Four kinds of lumber were used in the construction, representing four of the most common varieties used for house building, and were securely nailed to studding set 1 foot and 8 inches apart. The structure was divided off into sections 16 inches wide and 5 feet in length, giving sufficient surface for the careful brushing out of the paint; each type of paint being applied over the four kinds of wood, and the work being three coats in each case. Twenty-one mixed paints and white leads were applied on this fence, representing prevailing types of combinations.

Figure 7 represents a second series of exposure tests begun during the summer of 1907. These fences are like the one described above, except that they are each 100 feet in length. There is a four-inch air-space between the two surfaces of each fence; the numerous crevices between the boards permit of free circulation of air, and insures the prevention of continued dampness on the inside of the structure. Figure 8 illustrates the framework to which the boards and siding were nailed.

142. A more convenient method for making exposure tests, the painting of which may be done in the laboratory, is illustrated in Fig. 9. These test frames, so-called, have the additional merit of being easily transported from one place to another for inspection. These frames are 3 feet in length and 16 inches in width, the edge of the upper clapboard projecting half an inch above the cleats, and the lower clapboard set out a little, so that two or more

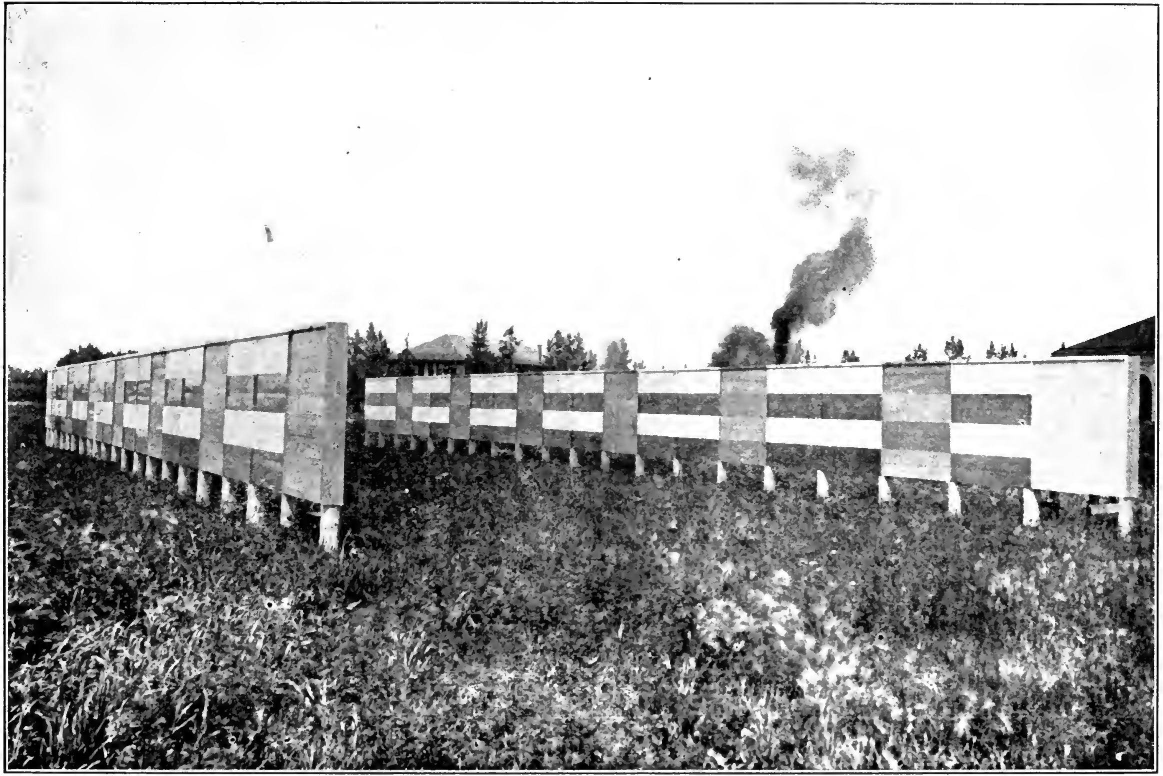

FIG. 7. EXPOSURE FENCES, 1907.

Fig. 8. Framework of Test Fences.

frames may be put together forming a unit surface, exactly similar to the side of a house. These frames are made to be screwed to a framework like that illustrated in Fig. 8. The clapboards, four in number, are set four inches to the weather, and are of two kinds of wood. The arrangement of the back cleats *a*, *a*, *a* and the end strips *b*, *b* through which the screws are inserted to hold the frame to the skeleton fence, are clearly shown in the illustrations.

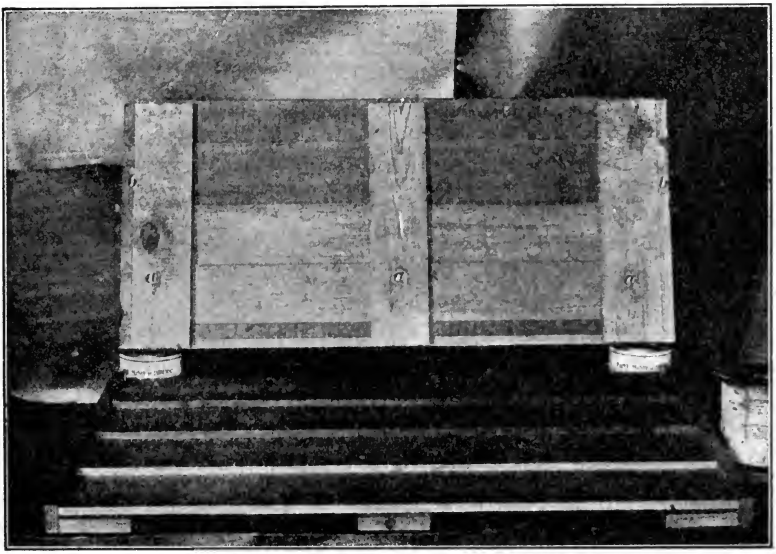

FIG 9. PORTABLE TEST FRAMES.

These end strips serve a much more important purpose, and one which makes the tests much more valuable than on a plain board surface, in that it tests out the brushing qualities of the paint very thoroughly. A poor paint will often brush out satisfactorily on an ordinary flat section of board, but will at once show its inferior quality when the painter attempts to work it into the corners and brush it away from the end strips, on the clapboard surface. In fact, it closely reproduces the actual conditions which the painter would encounter in applying the paint on an average house.

143. **Application of the priming coat.** In order to secure the best results with any given paint, three coats should be applied; of these three the most important is the priming coat. It compares with the foundation of a house, which, if not solidly and firmly constructed, renders the whole superstructure unstable. The priming coat, if not bedded thoroughly in the wood, will not serve to anchor and firmly bind the two additional coats to the surface. The essential consideration with the priming or first coat is to secure suitable penetration into the wood. In other words, the wood must be thoroughly satisfied. The necessity of this is explained with great force and clearness by J. B. Campbell, in his work entitled "Practical Painting."

144. The paint to be tested out if of the ready mixed type should be thoroughly "broken up," first pouring off the oil portion, stirring the residue until free from lumps, and then gradually working the oil portion back into the paste. This is best accomplished by removing the entire contents of the can into a larger mixing can, kept solely for this purpose. The consistency of the paint after being "broken up" should be carefully noted, whether it is thin, medium, or heavy, as the amount of reduction which the paint will stand depends largely on its consistency.

145. Raw linseed oil should almost without exception be used instead of boiled oil for reducing the paint for the priming coat. Raw oil dries slowly and from the bottom up, which allows it to be thoroughly absorbed and to harden uniformly. Boiled oil does not penetrate the wood, owing to its rapid drying qualities, and hence the coating formed is a surface coating only, and does not become

firmly anchored to the wood. Turpentine should be used liberally in the priming coat, as, by reducing the specific gravity and rendering the oil more mobile, it assists it in penetrating into the deeper pores of the wood; thus securing increased penetration and also more rapid drying. The harder and closer grained the wood, the larger the amount of turpentine required.

146. The following oil and turpentine reductions[1] will enable the chemist to judge the reduction required in most cases.

147. Oil reductions. "A full oil reduction consists of oil only, with the exception of $\frac{1}{32}$ gallon of turpentine, to the gallon of paint, to assist in penetration; this is not enough turpentine to destroy the lustre of the paint, and will accomplish the purpose of penetrating a hard or glossy surface, where it would be unsatisfactory to apply paint without the addition of a small percentage of this thinner.

148. "A liberal oil reduction consists of $\frac{7}{8}$ oil and $\frac{1}{8}$ turpentine to form the total amount of reducers; this amount of turpentine will cause more rapid and even penetration, but will not destroy the lustre of heavy-bodied paint.

149. "A medium oil reduction consists of $\frac{3}{4}$ oil and $\frac{1}{4}$ turpentine to form the total amount of reducers; this amount of turpentine will destroy part of the lustre and cause deep penetration on a hard surface.

150. "**Turpentine reductions.** A full turpentine reduction consists of nothing but turpentine, and is used for producing a flat paint.

151. "A liberal turpentine reduction consists of $\frac{7}{8}$ turpentine and $\frac{1}{8}$ oil, to form the total amount of reducers.

152. "A medium turpentine reduction is half turpentine and half oil.

153. "Dark shades require more turpentine to produce

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[1] Campbell, Practical Painting, p. 63.

the same results, as to penetration and flattening the paint, than light shades. Zinc and combination paints require more turpentine than strictly pure lead to produce the same results, as to destroying the lustre of the paint. Where light shades require $\frac{1}{8}$ gallon of turpentine to produce the desired results as to flattening or destroying the lustre and secure penetration, dark shades require $\frac{3}{16}$ of a gallon to produce like results."

154. It is also well to remember in making the reduction that turpentine reduces twice as fast as raw oil. The consistency to which the paint should be reduced for priming must necessarily be left to the judgment of the person applying it, and hence no definite directions can be given, but the following directions given by Campbell[1] have been found very helpful by the author.

155. "In priming soft wood, the paint should be applied with a full brush, and enough paint used at all times to satisfy the surface. It should be well brushed, and especially on the harder grain, to assist or force the paint into this close grain, and remove by hard brushing, any surplus paint that remains on the surface. On hard or close grained wood a medium full brush should be used in applying the paint, as this class of wood does not possess the absorbing properties of softer woods, but requires more brushing in order to force a sufficient amount of oil and binder into the wood and at the same time not leave an excess of paint on the surface.

156. "If the priming coat is of the proper consistency, carrying sufficient pigment to fill and hide the grain, and well brushed into the wood, most of the absorption will have ceased with this coat and no excess of pigment left on the surface. This thin coat will allow the second coat to penetrate through and satisfy any part of the wood

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[1] Practical Painting, p. 68.

which was not fully filled at the time of priming, and also allow the second coat to bind itself to the wood and priming coat."

157. Application of the middle coat. The priming coat should be given ample time to dry before applying the second coat, which, as Mr. Campbell states with much truth, should be " considered the medium between the foundation coat and the protecting or finishing coat." Careful judgment should be exercised in preparing the paint for this coating. " It must not be too elastic, and should dry firm without a high gloss. Too heavy an oil reduction will leave a high, glossy surface, over which the finishing coat will not adhere or properly dry." Sufficient turpentine should be used to secure the necessary penetration into the priming coat and to " flatten " out the paint so that it will show little or no gloss after 48 to 72 hours. Over such a surface, the finishing coat can be applied evenly, smoothly, and with great adherence. The directions for application as issued by most paint manufacturers are apt to fall short in the amount of turpentine necessary for the proper application of the second coat.

158. Nail holes and cracks should be carefully puttied. Cheap putty should be avoided, as it is apt to turn yellow and ultimately crumble and fall out. It is often better for the paint chemist to make his own putty, using medium whiting, raw oil and paste white lead to about 20 per cent of the whiting used. The mixture should be carefully kneaded and worked until of stiff consistency.

159. If the work is to be only two-coat, the paint should have a full oil reduction, so as to insure sufficient elasticity and opacity, and should be worked out well under the brush.

160. Application of third coat. The paint for this coat should be of good consistency, with a full raw oil reduction, so that it may be brushed out smoothly and evenly, and be sufficiently elastic so as to withstand severe exposures. Too much importance cannot be placed on the thorough brushing of the paint, as the durability and protection it affords are dependent to a great extent upon the thoroughness with which this is done. Paint flowed on will soon crack and come off, while, if plenty of muscle is used, it will make the finishing coat adhere more firmly to the second coat.

161. Application of paste leads and paste paints. In testing out paste paints and leads some convenient method should be adopted for calculating the amount of oil used in gallons per hundred pounds of paste. One of the simplest schemes is to weigh out the leads or pastes in 12½ oz. quantities or multiples thereof. Then each ounce of oil used is equivalent to one gallon per hundred pounds of paste.

One gallon is equivalent to 128 oz.

One hundred pounds are equivalent to 1600 oz.

$$1600 \div 128 = 12.5$$

In this way the necessary quantities of turpentine and drier can be rapidly calculated and measured out. For instance, if a specification to be tested out read,

100 lbs. white lead
7 gal. raw linseed oil
½ gal. turpentine
⅛ gal. turpentine drier,

the above scheme would call for

12½ oz. white lead
7 oz. raw linseed oil
½ oz. turpentine
⅛ oz. turpentine drier.

If larger amounts were required, the necessary multiple of 12½ should be used and the other figures increased accordingly.

162. **Driers.** The proper use of driers is often a perplexing problem with the paint chemist. Campbell[1] says: "A wide experience with the products as used by the painter shows the greatest possible difference between them. Some of them are sufficiently powerful so that even 5 per cent added to raw oil is enough to cause it to dry as fast as with boiled oil, and not only that, but to dry throughout or from the bottom up, and not merely surface dry, as will boiled oil. Others again are so loaded with rosin and petroleum products and so deficient in true drying properties that 25 per cent or more is required to accomplish this result, and then the resulting surface will be spongy or brittle, as the case may be, but in any event lacking in durability." In the face of these conditions the only recourse left the chemist, is to test out his driers thoroughly as described in a later chapter.

163. "The Japan or drier should be mixed with the paint while it is in semi-paste form. The mixing is thus uniform and the results satisfactory. If an attempt is made to add it after the paint is ready for the brush, the Japan is liable to curdle; it will be difficult to mix uniformly and the resulting work liable to be spotted, drying flat in some places and glossy in others." It should be borne in mind that paints containing zinc or dark colors will require more Japan than white lead alone, provided that it is essential to dry in a given time.

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[1] Practical Painting, p. 66.

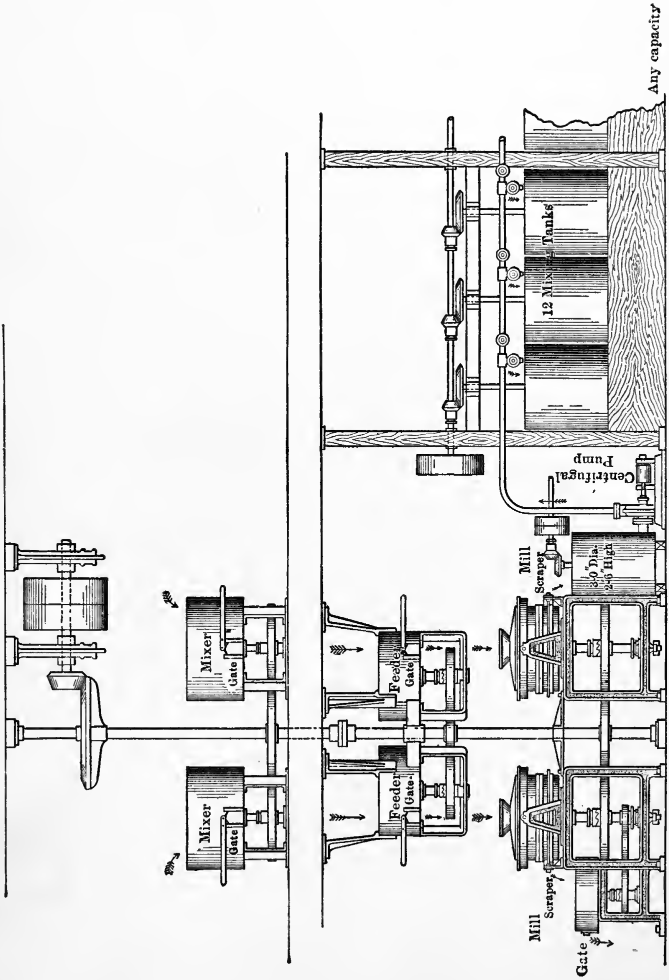

FIG. 10. TYPICAL WHITE LEAD AND MIXED PAINT OUTFIT. COURTESY OF KAESTNER & CO.

CHAPTER X.

ANALYSIS OF WHITE PAINTS.

164. Qualitative analysis of white paints. *Carbonates.* Effervescence with concentrated hydrochloric acid indicates carbonates, or hydrogen sulphide if zinc sulphide be present.

Barytes, silica, clay, or other silicates. Boil above mixture 5 minutes, dilute with boiling water, filter. An insoluble residue may be barytes, silica, clay or other silicates. Test for barytes with flame test, using a platinum wire.

Sulphates. Test a small portion of the acid filtrate for combined sulphuric acid with a few drops of barium chloride.

165. Lead. Test another small portion of the acid filtrate with sulphuric acid. A white precipitate indicates lead.

Zinc. Take another small portion of the acid filtrate and add a few drops of potassium ferrocyanide. A white precipitate with a bluish tinge indicates zinc.

Calcium. The remaining portion of the acid filtrate is made alkaline with ammonia and saturated with hydrogen sulphide for 5 minutes. Filter and test filtrate for calcium, with ammonium oxalate, setting aside in a warm place.

Magnesium. After completely precipitating the calcium, add a few drops of hydrogen sodium phosphate. A precipitate on standing, indicates the presence of magnesium compounds.

Quantitative Analysis of White Paints.

166. **Total lead.** Weigh 1 gram of the dry pigment into a 250 c.c. beaker. Add 30 c.c. of strong hydrochloric acid, boil 5 minutes, add 50 c.c. of hot water, heat 15 minutes longer, settle, filter while hot, and wash thoroughly with boiling water. Casein and other products of a similar nature are occasionally used in the manufacture of mixed paints in considerable quantities, and the analyst should always be on the lookout for the possible presence of these substances.

The solution is made just alkaline with ammonia, then just acid to litmus with hydrochloric acid; dilute to about 350 c.c. Cool, pass in hydrogen sulphide gas, noting the color of the precipitate; if gray, some zinc is being thrown down; if reddish black, the solution is too acid; add a few drops of dilute acid or ammonia as the case requires. Settle, filter, and wash with cold water. Digest, filter and precipitate in warm, dilute nitric acid, until the lead is completely dissolved. Filter on suction funnel, wash with boiling water, add 5 c.c. of dilute sulphuric acid to filtrate, and evaporate until sulphur trioxide fumes appear. Cool, add 25 c.c. of water, 25 c.c. of alcohol; allow to stand one-half hour with occasional stirring; filter, using Gooch crucible, wash with dilute alcohol, dry, heat gently over ordinary lamp, and weigh as lead sulphate.

167. **Calcium.** The filtrate containing the zinc, calcium and possibly magnesium is made slightly alkaline with ammonia, heated to the boiling-point and a stream of hydrogen sulphide gas passed into the solution for about 10 minutes. Add 5 grams ammonium chloride, boil 10 minutes. This treatment renders the precipitate less slimy. Settle, decant, filter, and wash. Reject precipitate.

Evaporate the filtrate from above precipitate to about

150 c.c., make alkaline with ammonia, add ammonium oxalate (50 c.c. for 1 gram of lime), usually 20 c.c. is sufficient, and set in a warm place for 2 or 3 hours. Filter, wash, ignite, and weigh as calcium oxide, or titrate precipitate with permanganate, as described under analysis of the calcium carbonate pigments. Barium carbonate is still to be found in certain mixed paints, and it is advisable to test for the presence of soluble barium before precipitating the calcium.

168. **Magnesium.** The filtrate from the calcium oxalate should be tested for magnesium, and if found, estimated in the usual manner.

169. **Zinc oxide.** Dissolve 1 gram of pigment in dilute hydrochloric acid, boil, dilute to about 200 c.c. and heat to about 80° C. Add about 3 grams of solid ammonium chloride, and titrate with standard potassium ferrocyanide, using uraninum acetate or nitrate as the indicator. Placing a drop of the indicator on a porcelain plate and adding 1 drop of solution, the formation of a brownish precipitate indicates the end point. Sufficient time should be allowed for the color change to take place. If the percentage of lead is considerable, add 3 drops of sulphuric acid before titrating.

The ferrocyanide solution is obtained by dissolving 43.2 grams in one litre, and titrating against a standard zinc solution obtained by dissolving 10 grams of pure zinc in hydrochloric acid, adding 50 grams of ammonium chloride, and making to one litre. This method has been often criticised as inaccurate, but if the titrations of the sample and of the standard zinc solution are made under exactly the same conditions as regards acidity, temperature, and concentration, the author believes that the results obtained will be entirely satisfactory.

170. **Lead sulphate.** Dissolve 0.5 gram in water

25 c.c., ammonia 10 c.c., hydrochloric acid in light excess.

Dilute to 200 c.c. and add a piece of aluminum foil which should about cover the bottom of the beaker. It is important that this be held at the bottom by a glass rod. Boil gently until the lead is precipitated. Completion of this is shown by the lead ceasing to coat or cling to the aluminum. Decant through a filter, pressing the lead sponge into a cake to free it from solution. Add to filtrate a little sulphur-free bromine water, boil until the bromine is expelled, add 15 c.c. of barium chloride, boil 10 minutes, filter, wash with hot water, ignite, and weigh as barium sulphate. Calculate to lead sulphate by multiplying by 1.3 as a factor, unless calcium sulphate is present, in which case it is advisable to make use of Thompson's separation, section 177.

In the absence of barium sulphate, the combined sulphuric acid may be estimated by H. Mannhardt's method: Triturate 1 gram of pigment with 1 gram of sodium carbonate, very intimately in an agate mortar. Boil gently for 10 minutes the combined sulphuric acid, and in the case of colors containing chromates, the chromic acid will be almost if not entirely extracted, and may then be estimated in the filtrate in the usual manner. If necessary collect the insoluble portion on a filter, dry, detach and triturate a second time.

171. Basic carbonate of lead. (White lead.) After deducting the amount of lead present in the pigment as sulphate of lead, calculate the rest of the lead as white lead by multiplying the remaining sulphate by 0.852, unless sublimed lead is suspected to be present; in which case, estimate the sublimed lead by the method described in section 84, and then calculate any remaining lead to the basic carbonate of lead.

172. The insoluble residue, from 166, may contain barytes, magnesium silicate, silica and clay. Ignite filter and residue until white, weigh as total insoluble matter; grind in agate mortar with about 10 times its weight of sodium carbonate, fuse for 1 hour in a platinum crucible, and dissolve out in hot water.

173. Barium sulphate. The solution from the fusion is filtered. The residue consists of barium carbonate, magnesium carbonate, etc., and is washed with hot water. The filtrate and washings are saved. Pierce filter paper and wash precipitate into clean beaker, wash with hot dilute hydrochloric acid, finish washing with hot water, heat to boiling, add 10 c.c. of dilute sulphuric acid to precipitate barium, filter, ignite, and weigh as barium sulphate.

174. Silica. The filtrate from the barium sulphate is added with care to the filtrate reserved in 173, making distinctly acid; evaporate to complete dryness, cool, add 15 c.c. of hydrochloric acid, and again evaporate to dryness and heat gently. Again dissolve in 50 c.c. of water, acidify with hydrochloric acid, heat to boiling, cool, settle, filter, ignite, and weigh as silica.

175. Alumina. The filtrate from the silica will contain all of the alumina except that which was dissolved in 166, with hydrochloric acid. This is quite constant, varying from .004 to .005 gram per gram of clay. The acid filtrates are made slightly alkaline with ammonia, and boiled until odor of ammonia disappears. Settle, filter, wash, ignite, and weigh as alumina.

$$\text{Wt. alumina} \times 2.5372 = \text{wt. clay.}$$
$$\text{Wt. clay} \times .4667 = \text{wt. of silica in clay.}$$

Any difference greater than 5 per cent may be considered as free or added silica, according to Scott.

176. Calcium and magnesium oxides. If qualitative test shows presence of magnesium in insoluble residue from 166 it was present probably as magnesium silicate. Treat filtrate from 175 for calcium and magnesium in usual manner, calculating results to calcium and magnesium oxides.

Magnesium silicate contains 3–5 per cent combined water and about 60 per cent silica.

177. **Mixed carbonates and sulphates.** Occasionally paints are met with which contain calcium sulphate, calcium carbonate, sulphate of lead and white lead (basic carbonate of lead), in which case it is necessary to make a separation of the calcium compounds, which may be effected by Thompson's method as follows:

To 1 gram of the sample are added 20 c.c. of a mixture of 9 parts alcohol (95 per cent) and 1 part of concentrated nitric acid. Stir, and allow to stand 20 minutes. Decant on a filter and repeat the treatment with the acid-alcohol mixture 4 times, allowing it to stand each time before decanting. The calcium carbonate will go into solution, while the calcium sulphate or gypsum remains undissolved. Add filter and contents to the residue remaining in the beaker; dissolve in hydrochloric acid with sufficient water to insure the solution of the calcium. Make alkaline with ammonia, pass in hydrogen sulphide for 10 minutes, boil, settle, filter. The filtrate and washings are concentrated to about 150 c.c. and the calcium precipitated with ammonium oxalate in the usual manner. The ignited precipitate is calculated to hydrated calcium sulphate.

178. **Calculations.** The ignited precipitate of calcium oxide obtained from the portion insoluble in the acid alcohol mixture is subtracted from the total calcium weighed as oxide; the remaining calcium oxide is calculated to calcium carbonate. The total carbon dioxide is determined in a portion of the sample, the portion due to the calcium

carbonate is deducted from the total amount, and the remainder calculated to basic carbonate of lead. The combined sulphuric acid due to the sulphate of lime is deducted from the total combined sulphuric acid, and the remainder calculated to sulphate of lead.

Wt. calcium oxide × 3.0715 = hydrated calcium sulphate.

Wt. calcium oxide × 1.784 = calcium carbonate.

Wt. calcium carbonate × 0.440 = carbon dioxide.

Wt. carbon dioxide × 8.8068 = basic carbonate of lead.

Wt. of hydrated sulphate of lime × 0.4561 = combined sulphuric acid.

Wt. of combined sulphuric acid × 3.788 = sulphate of lead.

179. TYPICAL ANALYSES OF MIXED PAINTS.[1]

	I.	II.	III.	IV.
Color	Stone.	Lead.	Gray.	White.
Can	1.00 qt.	4.06 qt.	1.06 qt.	1.08 qt.
Contents	.90 qt.	4.01 qt.	1.05 qt.	.93 qt.
Net weight	2 lbs. 14 oz.	16 lbs. 3 oz.	4 lbs.	3 lbs. 4 oz.
Vehicle	50.1	34.2	38.2	36.9
Pigment	49.9	65.8	61.8	63.1
	100.00	100.00	100.00	100.00

ANALYSIS OF VEHICLE.

	I.	II.	III.	IV.
Linseed oil	68.9	90.4	90.6	89.6
Benzine drier	16.1	...	3.4	10.1
Turpentine drier	...	9.4	4.0	...
Water	15.0	0.2	2.0	0.3
	100.00	100.00	100.00	100.00

ANALYSIS OF PIGMENT.

	I.	II.	III.	IV.
White lead	21.73	49.53	16.64	21.56
Lead sulphate	0.85	0.44	13.48	1.09
Zinc oxide	47.89	49.64	39.80	49.25
Calcium carbonate	21.98	...	10.68	1.80
Barytes	...	...	18.93	...
Silica	5.41	...	...	...
Magnesium silicate,	...	...	...	25.87
Color, undetermined, etc.	2.14	0.39	0.47	0.43
	100.00	100.00	100.00	100.00

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[1] Analyses made by author.

180. No. 1 is a fair type of a large number of mixed paints, short in volume, short in weight, low in pigment, nearly one-third of the vehicle being benzine and water, and 27 per cent of total pigment inert material.

No. 2 is a strictly first-class paint in every respect, full measure, 16 lbs. to the gallon, pure turpentine drier and high white lead content.

No. 3 is full measure and full weight. The percentage of drier is well within the usually accepted limits, but the manufacturer obtains a considerable relief by the use of nearly 30 per cent of inert pigments costing only a small fraction of the price of white lead or zinc. This paint also has a very small percentage of added water.

No. 4 is 7 per cent short in volume, is low in lead pigments, and contains nearly 28 per cent of inert pigment, which in this case is mainly magnesium silicate.

181. Calculation of the approximate cost of mixed paints using No. I and No. II as types.

COST OF VEHICLE.

Liquid.	Cost per Gallon	No. I.		No. II.	
		Gal.	Total Cost.	Gal.	Total Cost.
Linseed oil	$ 0.40	68.9	$27.56	90.4	$36.16
Turpentine drier	1.00	...	...	9.4	9.40
Benzine drier	0.0326	16.1	5.25	...	...
Water	0.00	15.0	0.00	0.2	...

100 gallons (750 pounds). No. I, cost $32.81.
1 pound costs $0.0438.
50.1 pounds cost $2.19.
100 gallons (750 pounds), No. II, costs $45.56.
1 pound costs $0.0607.
34.2 pounds cost $2.09.

COST OF PIGMENT.

Pigment.	Cost per Lb.	No. I.		No. II.	
		Lbs.	Total Cost.	Lbs.	Total Cost.
White lead	$0.065	21.73	$1.41	49.53	$3.22
Lead sulphate[1]	0.05	0.85	0.04	0.44	0.02
Zinc oxide	0.05	47.89	2.39	49.64	2.48
Inert pigments	0.01	27.39	0.27	...	...
Color	0.05	2.14	0.11	0.47	0.02

100 pounds total pigment, No. I, cost $4.22.
1 pound costs $0.042.
49.9 pounds cost $2.11.

100 pounds total pigment, No. II, cost $5.74.
1 pound costs $0.057.
65.8 pounds cost $3.75.

No. I.

50.1 pounds liquid cost	$2.19
49.9 pounds pigment cost	2.11
100.0 pounds paint cost	$4.30
1.0 pound paint costs	0.043
1 gallon (2 pounds 14 ounces) × 4 costs	0.495

No. II.

34.2 pounds liquid cost	$2.09
65.8 pounds pigment cost	3.75
100.0 pounds paint cost	$5.84
1 pound paint costs	0.0584
1 gallon (or 16 pounds 3 ounces) costs	0.945

In other words, one paint costs almost exactly twice as much as the other, as regards paint and oil ingredients. The cost of the can (gallon size), label, and crate is about 10 cents. Salesmen's commissions, salary and travelling expenses are about 5 cents per gallon; the cost of manufacture, depreciation of plant and machinery, 6 to 8 cents per gallon.

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[1] Lead sulphate present in the zinc oxide.

It must also be borne in mind that the cost of crude materials has advanced markedly during the last few years. The following table prepared by the Paint Manufacturers' Association shows the increase in cost of various paint materials in 1907, as compared with 1897.

Material.	Per cent Increase in Cost.
White lead	61.8
Zinc oxide	40.5
Barium sulphate	44.2
Linseed oil	45.4
Turpentine	155.0
Japan drier	42.0
Tin cans	33.0
Packing boxes	64.2

182. ANALYSES OF SUBLIMED LEAD PAINTS BY AUTHOR.

	I. White.	II. White.	III. Pearl Gray.	IV. White.
Net weight, lbs. and oz.	15	15:1	14:8	3:20
Capacity of can, qts.	3.96	4.00	4.00	1.03
Contents, qts.	3.95	3.94	3.86	.95
	Per cent.	Per cent.	Per cent.	Per cent.
Pigment by weight	57.0	59.2	58.6	64.8
Vehicle by weight	43.0	40.8	41.4	35.2
	100.0	100.0	100.0	100.0

Analysis of Vehicle.

	Per cent.	Per cent.	Per cent.	Per cent.
Linseed oil	90.5	90.4	90.4	84.5
Drier	9.3[1]	9.5	9.6	6.4
Water	0.2	0.1	0.0	9.1
	100.00	100.00	100.00	100.00

Analysis of Pigment.

	Per cent.	Per cent.	Per cent.	Per cent
White lead	0.00	0.00	0.00	0.00
Lead sulphate[2]	58.37	33.46	35.56	59.09
Lead oxide	5.99	9.63	8.93	16.01
Zinc oxide	35.24	56.38	55.11	5.18
Barium sulphate	0.00	0.00	0.00	19.08
Undetermined color, etc.,	0.40	0.53	0.40	0.64
	100.00	100.00	100.00	100.00

[1] Benzine.

[2] Sublimed lead.

In the above analyses the percentage of zinc oxide incidental to the manufacture of sublimed lead is included in the total zinc oxide.

183. ANALYSES OF LEADED ZINC PAINTS BY AUTHOR.

	I. Lead Color.	II. White.	III. Blue.	IV. Gray.
Net weight, lbs. and oz.	6:14	3:8	0:14.5	5:10
Capacity of can, qts.	1.91	1.06	.33	1.95
Contents, qts.	1.82	1.00	.28	1.70
	Per cent.	Per cent.	Per cent.	Per cent.
Pigment by weight	58.9	60.7	57.0	57.8
Vehicle by weight	41.1	39.3	43.0	42.2
	100.00	100.00	100.00	100.00

ANALYSIS OF VEHICLE.

	I.	II.	III.	IV.
Linseed oil	80.2	56.9	60.4	77.6
Benzine drier	8.5	20.6	25.7	7.9
Water	11.3	22.5	13.9	14.5
	100.00	100.00	100.00	100.00

ANALYSIS OF PIGMENT.

	Per cent.	Per cent.	Per cent.	Per cent.
White lead	...	...	...	...
Lead sulphate	39.26	18.13	17.77	14.23
Zinc oxide	34.20	34.04	33.58	37.57
Calcium carbonate	5.39	41.09	39.88	41.70
Barytes	19.90	6.20	6.40	6.10
Undetermined color, etc.	1.25	0.54	2.37[1]	0.40
	100.00	100.00	100.00	100.00

184. ANALYSES BY AUTHOR OF MIXED PAINTS FOR INSIDE USE.

	I. Inside White.	II. Inside White.	III. Inside White.
Net weight, lbs. and oz.	3:0	15:0	14:2
Capacity of can, qts.	1.04	0.30	0.30
Contents, qts.	0.99	0.26	0.24
	Per cent.	Per cent.	Per cent.
Pigment	62.9	28.3	62.8
Vehicle	37.1	71.7	37.2
	100.00	100.00	100.00

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[1] Color largely organic.

VEHICLE.

	Per cent.	Per cent.	Per cent.
Linseed oil	60.1[1]	68.6[1]	77.9
Turpentine	39.9	30.0	22.1
Water	0.0	1.4	0.0
	100.0	100.0	100.0

PIGMENT.

		Per cent.	Per cent.	Per cent.
White lead		...	...	18.84
Lead sulphate		2.57	...	...
Zinc oxide		70.27	99.80	80.45
Lithopone		26.33	...	...
Barium sulphate	20.12		...	...
Zinc sulphide	6.13		...	...
Silica		0.28	...	...
Undetermined		0.55	0.20	0.71
		100.00	100.00	100.00

185. Analyses of cheapened mixed paints by the author, showing the various devices used for cheapening the cost of production, — short volume, low pigment content, practical absence of all lead pigments, excessive use of drier, high per cent of water and of cheap inert pigments. Two of these brands were sold as straight white lead and zinc oxide paints.

	I. White.	II. Gray.	III. Lead Color.	IV. Slate Color.
Net weight, lbs. and oz.	3:0	6:3	9:9	5:12
Capacity of can, qts.	1.03	1.95	3.37	1.90
Contents, qts.	.99	1.92	2.42	1.85

	Per cent.	Per cent.	Per cent.	Per cent.
Pigment by weight	55.1	54.6	67.10	50.8
Vehicle	44.9	45.4	32.90	49.2
	100.0	100.0	100.00	100.0

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[1] Includes a small amount of dammar varnish.

ANALYSIS OF VEHICLE.

	Per cent.	Per cent.	Per cent.	Per cent.
Linseed oil	72.5	54.4[1]	83.9[1]	61.9
Benzine drier	9.1	28.9	4.3	22.0
Water	18.4	16.7	11.8	16.1
	100.00	100.00	100.00	100.00

ANALYSIS OF PIGMENT.

	Per cent.	Per cent.	Per cent.	Per cent.
White lead	...	...	...	...
Lead sulphate	.89	3.11	4.73	0.74
Zinc oxide	53.86	24.67	24.34	60.10
Calcium carbonate	43.39	40.07	4.47	21.11
Magnesium carbonate	0.73	...	...	...
Barytes	...	22.10	66.26	...
Silica	0.60	7.26	...	16.25
Undetermined color, etc.	.53	2.79	0.20	1.80
	100.00	100.00	100.00	100.00

ANALYSIS OF WHITE PAINTS ACCORDING TO THOMPSON.[2]

186. Schemes for the separation of the constituents from each other and into their proximate combinations depend on the constituents present, and we can treat this subject in no better way than by taking typical cases, which we now do.

187. *Sample* 1 is a mixture of barytes, white lead, and zinc oxide.

Two 1-gram portions are weighed out. One is dissolved in acetic acid and filtered, the insoluble matter ignited and weighed as barytes, the lead in the soluble portion precipitated with bichromate of potash, weighed in Gooch crucible as chromate, and calculated to white lead.

The other portion is dissolved in dilute nitric acid, sulphuric acid added in excess, evaporation carried to fumes, water added, the zinc sulphate solution filtered

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[1] Very low grade linseed oil.

[2] J. Soc. Chem. Ind., June 30, 1896.

from barytes and lead sulphate and precipitated directly as carbonate, filtered, ignited, and weighed as oxide.

188. *Sample* 2 is a mixture of barytes and so-called sublimed white lead.

Weigh out three 1-gram portions. In one determine zinc oxide as in case 1. Treat a second portion with boiling acetic acid, filter, determine lead in filtrate and calculate to lead oxide. Treat third portion by boiling with acid ammonium acetate, filter, ignite, and weigh residue as barytes, determine total lead in filtrate, deduct from it the lead as oxide, and calculate the remainder to sulphate. Sublimed lead contains no hydrate of lead, and its relative whiteness is probably due to the oxide of lead being combined with the sulphate as basic sulphate. Its analysis should be reported in terms of sulphate of lead, oxide of lead, and oxide of zinc.

189. *Sample* 3 is a mixture of barytes, sublimed lead, and white lead.

Determine barytes, zinc oxide, lead soluble in acetic acid and in ammonium acetate, as in case 2; also, determine carbonic acid, which calculated to white lead, deduct lead in white lead from the lead soluble in acetic acid, and calculate the remainder to lead oxide.

190. *Sample* 4 is a mixture of barytes, white lead, and carbonate of lime.

Determine barytes and lead soluble in acetic acid (white lead) as in case 1. In filtrate from lead chromate precipitate lime as oxalate, weigh as sulphate, and calculate to carbonate. Chromic acid does not interfere with the precipitation of lime as oxalate from acetic acid solution.

191. *Sample* 5 is a mixture of barytes, white lead, zinc oxide, and carbonate of lime.

Determine barytes and white lead as in case 1. Dissolve another portion in acetic acid, filter and pass sulphuretted hydrogen through the boiling solution, filter, and precipitate lime in filtrate as oxalate; dissolve mixed sulphides of lead and zinc in dilute nitric acid, evaporate to fumes with sulphuric acid, separate, and determine zinc oxide as in case 1.

192. *Sample* 6 is a mixture of barytes, white lead, sublimed lead, and carbonate of lime.

Determine barytes, lead soluble in acetic acid and in ammonium acetate, as in case 2, lime and zinc oxide, as in case 5, and carbonic acid. Calculate lime to carbonate of lime, deduct carbonic acid in it from total carbonic acid, calculate the remainder of it to white lead, deduct lead in white lead from lead soluble in acetic acid, and calculate the remainder to oxide of lead.

193. *Sample* 8 contains as insoluble matter, barytes, china clay, and silica.

After igniting and weighing the insoluble matter, carbonate of soda is added to it, and the mixture fused. The fused mass is treated with water, and the insoluble portion filtered off and washed. This insoluble portion is dissolved in dilute hydrochloric acid, and the barium present precipitated with sulphuric acid in excess. The barium sulphate is filtered out, ignited, weighed, and if this weight does not differ materially — say by 2 per cent — from the weight of the total insoluble matter, the total insoluble matter is reported as barytes. If the difference is greater than this, add the filtrate from the barium sulphate precipitate to the water-soluble portion of fusion. Evaporate and determine the silica and the alumina in the regular way. Calculate the alumina to China clay on the arbitrary formula $2SiO_2, Al_2O_3, 2H_2O$, and deduct the silica in it from the silica, reporting the latter in a free state. It is to be borne in mind that China clay gives a loss of about 13 per cent on ignition, which must be allowed for. China clay is but slightly used in white paints as compared with barytes and silica.

194. *Sample* 9 contains sulphide of zinc.

Samples of this character are usually mixtures in varying proportions of barium sulphate, sulphide of zinc, and oxide of zinc. Determine barytes as matter insoluble in nitric acid, the total zinc as in case 1, and the zinc soluble in acetic acid, which is oxide of zinc. Calculate the zinc insoluble in acetic acid to sulphide.

195. *Sample* 10 contains sulphite of lead.

This is of rare occurrence. Sulphite of lead is insoluble in ammonium acetate, and may be filtered out and weighed as such. It is apt on exposure to the air in the moist state to become oxidized to sulphate of lead.

There are certain arbitrary positions which the chemist must take in reporting analyses of white paints: —

1st. White lead is not uniformly of the composition usually given as theoretical ($2\,PbCO_3$), (PbH_2O_2), but in reporting we must accept this as the basis of calculating results, unless it is demonstrated that the composition of the white lead is very abnormal.

2d. In reporting oxide of lead present this should not be done except in the presence of sulphate of lead, and if white lead is present, then only where the oxide is more than one per cent; otherwise calculate all the lead soluble in acetic acid to white lead.

3d. China clay is to be calculated to the arbitrary formula given.

In outlining the above methods we have in mind many samples that we have analyzed, and the combinations we have chosen are those we have actually found present.

CHAPTER XI.

ANALYSIS OF INDIAN REDS, VENETIAN REDS, TUSCAN REDS, RED OXIDES, AND OCHRES.

196. Hygroscopic moisture. Heat 2 grams at 105° C. for 3 hours. Loss in weight represents hygroscopic moisture.

197. Combined water, etc. Transfer above sample to a weighed platinum crucible and heat for one hour over an ordinary lamp, or better in a muffle. Loss in weight indicates amount of combined water. Carbonates and organic matter render the results inaccurate, in which case continue the ignition at bright red heat for several hours, and weigh again. Determine the carbon dioxide in another portion of the sample and estimate the combined water by difference. If a large amount of calcium sulphate is present, it is possible to heat it strongly enough to partially drive off the combined sulphuric acid, and unless this be taken account of the analysis will total up to more than 100 per cent. In the case of a Tuscan red which has precipitated upon it an organic color, the loss in weight is best reported as combined water and organic matter. The presence of an organic color may always be detected by the characteristic odor given off at the beginning of the ignition.

198. Silica and barium sulphate. One gram of the pigment is intimately mixed with 6 to 8 grams of potassium bisulphate and fused in a large porcelain crucible, the cover of which is small enough to set inside the top of the crucible, at not too high a temperature for one-half hour, finally heating the side of the crucible to finish the conversion of any material adhering to the cover and upper portion of the crucible. The iron, aluminum, calcium, and magnesium are converted into sulphates, the barytes remains unchanged and the silica is completely dehydrated. With a little care, using a low heat at first, the fusion may be conducted with very little frothing or spattering. Fusion with bisulphate is to be preferred to solution with hydrochloric acid, as ferric chloride is appreciably volatile on boiling. Also the silicates of iron that are present in small quantity in the natural oxides are not decomposable with hydrochloric acid.

After cooling, the entire contents of the crucible may be shaken loose and dissolved in sufficient water and a little hydrochloric acid. Filter and make up to 250 c.c. unless calcium is present in large amount, in which case make up to a volume of not less than 500 c.c. as calcium sulphate is but sparingly soluble.

The residue remaining on the filter is ignited and weighed in a platinum crucible. The residue is tested for barium sulphate by the flame test: if absent the residue is reported as silica; if present the residue is treated in the crucible with hydrofluoric acid until a thin paste is formed. The mixture is stirred with a platinum wire and digested at a gentle heat; finally two or three drops of sulphuric acid are added, and the temperature gradually raised until no further loss in weight takes place, indicating that the silica has been completely expelled. The residue is weighed as barium sulphate, and the loss in weight represents the silica, or, the residue of barium sulphate and silica may be fused with sodium carbonate as described under the analysis of white pigments.

199. Ferric oxide. An aliquot portion of the solution from 198 is heated to boiling, and stannous chloride solution added cautiously until the yellow color has disappeared, and then a slight excess added. All at once with vigorous shaking of the flask, 50 c.c. of mercuric chloride solution is added, then 50 c.c. of the manganous sulphate solution. Dilute with cold fresh boiled water and titrate with permanganate solution. Calculate iron found to ferric oxide.

200. Preparation of Reagents.

a. Stannous chloride. Dissolve 30 grams of tin in 250 c.c. of hydrochloric acid, filter through glass wool, and make up to one litre.

b. Mercuric chloride. Dissolve 50 grams in one litre.

c. Manganous sulphate. One litre should contain 66.7 grams of crystallized manganous sulphate, 333 c.c. phosphoric acid (Sp. Gr. 1.3) and 133 c.c. of conc. sulphuric acid.

d. Potassium permanganate. Dissolve 3.16 grams in one litre; standardize against the standard iron solution.

e. Standard iron solution. Dissolve 7.03 grams iron wire, 99.7 per cent purity, in dilute hydrochloric acid; make to one litre.

1 c.c. = 0.01 g. ferric oxide or 0.007 gr. iron.

In many cases where a rapid commercial determination of the iron content alone is desired, the pigment may be dissolved in hydrochloric acid, with the subsequent addition of a few drops of nitric acid, filtered, the iron and alumina precipitated with ammonia; after thorough washing dissolved in sulphuric acid, run through a "reductor," such as may be obtained from any of the leading supply houses, and then simply titrated with standard permanganate solution in the usual manner.

201. Alumina. An aliquot part of the solution in 198 is made just alkaline with ammonia, boiled, decanted, filtered, washed, redissolved, reprecipitated, filtered, ignited and weighed as alumina and ferric oxide, the alumina being obtained by difference.

202. Calcium. The filtrate from the iron and alumina is treated with ammonium oxalate (50 c.c. is sufficient for one gram of calcium pigment). Set aside in a warm place for two or three hours, filter, ignite, and weigh as calcium oxide, or titrate with standard permanganate, as may be desired. The calcium may have been present as carbonate or sulphate or both. Hence an estimation of the sulphur trioxide present in the original sample is necessary. For this purpose 1 gram is dissolved in 30 c.c. of strong hydrochloric acid, boiled 10 minutes, diluted with 50 c.c. of water, heated to boiling, filtered, and washed with hot water. Neutralize the filtrate with ammonia, then make just distinctly acid with hydrochloric acid, boil, add 10 c.c. of barium chloride solution, continue boiling for 10 minutes, filter, wash, ignite and weigh as barium sulphate. Calculate sulphur trioxide by multiplying weight of precipitate by 0.343.

Calculate the sulphur trioxide found to calcium sulphate and the remaining calcium to oxide, provided that the carbon dioxide is included under loss on ignition. If desired, the remaining calcium may be calculated to calcium carbonate, the combined carbon dioxide being deducted from the loss on ignition.

203. Magnesium. If a considerable percentage of calcium is found, magnesium is liable to be present, precipitate with sodium hydrogen phosphate in usual manner. Calculate the pyrophosphate to oxide by multiplying by the factor 0.3624.

204. ANALYSES OF INDIAN REDS, RED OXIDES, AND VENETIAN REDS.[1]

	Insoluble.	Ferric Oxide.	Alumina.	Calcium Oxide.	Carbon Dioxide.	Magnesium Oxide.	Sulphur Trioxide.	Moisture.	Loss on Ignition.
Pure Indian Red	0.67	94.35	2.69	...	...	...	...	0.20	1.53
Pure Indian Red	0.48	96.93	1.10	...	...	...	...	0.41	0.90
Pure Indian Red	0.61	97.49	0.77	...	...	...	...	0.36	0.80
Superfine Indian Red	0.65	95.05	3.96	...	...	...	...	0.06	0.19
Imported Red Oxide	19.42	77.93	0.25	1.21	...	...	...	0.20	1.41
Ordinary Red Oxide	10.82	38.30	5.43	17.99	1.32	0.96	19.20	2.50	3.45
Red Oxide	11.55	53.95	12.03	9.33	...	0.68	1.55	0.01	10.95
Red Oxide	0.71	94.88	3.20	...	...	...	...	0.15	1.98
Red Oxide	13.61	70.15	2.09	6.12	1.45	...	5.85	0.13	1.23
Imported Red Oxide	1.33	29.22	1.76	23.19	...	0.30	37.00	5.47	2.52
Best Tuscan Red Oxide	0.64	59.09	1.20	15.27	...	0.40	23.15	0.01	0.81
Turkey Red Oxide	1.90	51.97	2.31	14.85	...	0.52	17.92	6.36	4.34
Turkey Red Oxide	15.74	64.00	6.15	5.88	...	0.48	0.20	0.06	7.25
American Venetian Red	55.92	35.64	1.71	2.90	...	...	...	0.44	3.94
American Venetian Red	20.36	16.78	2.35	18.66	27.19	12.06	2.45	0.10	...
Royal Venetian Red	1.82	9.00	0.57	30.47	39.40	18.26	...	0.30	...
Royal Venetian Red	2.10	20.83	2.42	31.65	7.22	1.34	28.70	3.50	2.79
Superfine Venetian Red	18.75	76.31	2.11	0.65	0.45	...	...	0.05	1.74
Light Brilliant Venetian Red	6.06	11.56	1.01	25.46	1.65	1.88	35.15	12.12	5.30
Imported Venetian Red	27.30	61.01	6.38	0.88	...	...	2.05	0.09	2.03
Venetian Red	1.07	9.50	0.28	45.00	12.06	0.50	25.00	6.84	...
Light Victoria Venetian Red	1.46	22.79	1.19	27.95	...	0.79	36.15	6.72	3.76
Windsor Venetian Red	18.85	24.43	1.84	26.89	13.14	1.33	11.15	2.17	...
V. C. Eng. Venetian Red	2.85	18.79	3.38	39.21	18.39	0.52	16.30	0.01	...
Home Imported Venetian Red	10.81	18.78	2.05	28.50	1.78	1.36	22.67	10.68	3.95
Cutter's English Venetian Red	0.30	22.00	1.79	29.03	...	...	34.90	7.51	3.44

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[1] Weems, Iowa, Eng. Soc., Jan. 1901.

205. Tuscan reds should contain about 60 per cent ferric oxide, and are often brightened up by having precipitated on them an organic red. Another class of oxides, carrying about the same amount of iron oxide as Tuscan reds, is "Prince's metallic." The variation of iron content is shown in the following analyses:

No.	Ferric Oxide.
I	44.07
II	38.17
III	68.45
IV	49.58
V	39.35

A complete analysis gave the following:

	Per cent.
Volatile	3.33
Ferric Oxide	40.91
Alumina	3.49
Calcium Oxide	2.00
Insoluble	49.57
Undetermined	0.70
	100.00

206. Ochres, of which the French ochres are considered the best, to pass inspection by the various service department scientists of the United States Government, must be of good bright color, contain at least 20 per cent sesquioxide of iron and not over 5 per cent of lime in any form. A good grade of yellow ochre to pass this inspection would analyze about as follows : —

	Per cent.
Silica	52.14
Alumina	12.89
Ferric oxide	22.42
Calcium oxide	0.36
Combined water	10.16
Hygroscopic water	2.03
	100.00

207. ANALYSES OF OCHRES AND IRON OXIDE PIGMENTS BY THE AUTHOR.

	Moisture.	Comb. H_2O and Loss on Ignition	Silica.	Ferric Oxide.	Alumina.	Calcium Oxide.	Magnesium Oxide.	Carbon Dioxide.	Sulphur Trioxide.	Barium Sulphate.	Undetermined.
Ochre B. F.	0.29	6.78	61.49	18.15	12.78	0.20	...	...	...	...	0.31
Ochre Clair	0.19	9.54	53.80	21.05	14.35	0.67	...	...	...	...	0.40
Ochre	0.18	8.70	52.63	23.01	15.34	...	...	...	...	...	0.14
Ochre	0.09	9.44	52.34	21.01	16.93	...	...	...	...	...	0.19
Ochre	0.85	6.60	62.00	24.96	5.29	...	...	...	...	...	0.30
Ochre J. F. L. S.	0.30	8.71	53.09	26.30	11.31	...	...	...	...	...	0.29
Ochre J. B. N. Y.	0.70	14.41	50.00	19.85	15.23	0.57	0.01	...	...	...	0.23
Venetian Red Med.	6.34	...	2.38	22.40	1.72	29.32	0.17	4.72	32.66	...	0.29
Venetian Red Med.	10.18	4.86	1.45	11.88	1.10	30.49	.02	6.32	32.54	...	0.16
Tuscan Red	0.06	...	38.38	25.08	...	20.87	...	14.78	...	...	0.83[1]
Tuscan Red	1.32	6.08	1.51	23.30	9.55	...	...	...	...	58.24	...
Tuscan Red	0.31	...	2.22	49.55	4.61	23.78	...	18.70	0.49	...	0.34
Oxide N.	0.05	3.03	8.25	85.82	1.99	...	...	...	...	...	0.83
Red Oxide.	0.01	0.23	46.30	39.72	11.28	0.99	1.24	...	...	...	0.23
Indian Red	0.13	1.24	1.14	94.61	2.65	...	...	...	...	...	0.23

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[1] Includes organic color.

Specifications for Venetian Red.

(Bureau of Supplies and Accounts, Navy Department, 1902).

208. Red, Venetian. I. Red, Venetian (bright). The dry pigment must contain at least 20 per cent of sesquioxide of iron, not more than 15 per cent of silica, the balance to consist of sulphate of lime that has been fully dehydrated by dead burning, and rendered incapable of taking up water of crystallization.

II. Red, Venetian (deep). The dry pigment must contain at least 30 per cent of sesquioxide of iron, not more than 15 per cent of silica, the balance to consist of sulphate of lime that has been fully dehydrated by dead burning and rendered incapable of taking up water of crystallization.

III. Red, Venetian (medium). The dry pigment must contain at least 40 per cent of sesquioxide of iron, not more than 15 per cent of silica, the balance to consist of sulphate of lime that has been fully dehydrated by dead burning and rendered incapable of taking up water of crystallization.

CHAPTER XII.

ANALYSIS OF BLACK AND BROWN PIGMENTS AND PAINTS.

209. Composition. The ordinary black pigments, lampblack, vegetable black, bone black, ivory drop black, gas black, graphite, etc., contain carbon as their essential constituent, and while all of these products are said to be of a black color, they vary greatly in shade and still more so in tinting strength.

1. Lampblack and vegetable black are essentially soot blacks, being the soot deposited from the combustion of oily bodies such as dead oil. Lampblack has a distinct gray tint as may be shown by comparison with ivory black. These blacks are apt to contain varying quantities of oil, owing to the nature of their manufacture. Less than 1 per cent of oil often being sufficient to retard seriously the drying of lampblack paints. Vegetable blacks are more voluminous than lampblacks and are usually of a jet black color.

2. Carbon black is usually produced from the incomplete combustion of natural gas. While its tinting power is very great its use has been largely abandoned owing to its tendency to produce a streaky color when used in tinting paints.

3. Bone black is as its name indicated, obtained by the charring of bones in retorts. The carbon content varies usually between 12 and 22 per cent, the balance consisting of moisture, phosphate of calcium and carbonate of calcium. The best grades of bone black are made from selected sheep bones. An exceedingly intense

black is made by digesting selected bones in hydrochloric acid until all of the mineral matter is dissolved, leaving the carbon in a flocculent state. This black is often sold under the name of black toner, and is one of the highest priced blacks.

4. Animal black is a name sometimes given to bone black but is also used to designate a wide variety of blacks prepared in the same way as bone black from waste animal products of all kinds, as leather scrap parings, horn trimmings, etc.

5. Frankfort black, drop-black and German black are terms used to designate blacks made from a variety of organic materials, such as vine twigs, refuse of wine-making, peach stones, bone shavings, etc. These blacks vary in hue from a bluish-black to a reddish-black.

6. Graphite while not used to any extent in house-paints is largely used in bridge, elevator, and warehouse paints. It is rarely used by itself for these purposes, silica, calcium carbonate and iron oxide pigments, zinc and lead being the other usual constituents. It may be tested for qualitatively in the extracted pigment by rubbing a portion of the sample between the palms, which soon assume the characteristic appearance produced by stove polish. Of all the black pigments graphite alone gives this test.

7. Charcoal black and vine black are produced by the charring of wood products, and contain besides carbon the ash ingredients common to wood. Charcoal blacks are usually made from maple, willow and bass wood, and vine blacks from the charring of the grape vine. Paints containing considerable quantities of these blacks are liable to saponify badly owing to the moisture and potash salts present.

8. Mineral black which is still occasionally used is black slate finely ground.

210. **Moisture.** Dry 2 grams at 105° C. for 3 hours. Loss in weight represents approximately the amount of moisture present.

211. **Oils.** Extract 2 grams with ether in a fat extraction apparatus. After removing the ether and drying, any increase in weight represents the amount of oily matter present.

212. **Ash.** Two grams are weighed into a crucible and heated over a Bunsen burner until all the carbon is burned off. If the ash constitutes only a small per cent, it may be cooled and weighed directly. Otherwise the residue is moistened with a solution of ammonium carbonate, heated gently, and weighed. The object of this operation is to restore the carbon dioxide which may have been expelled from the bases by the strong heat to which they have been subjected.

213. **Carbon.** The carbon is usually estimated by difference, by adding together the moisture, oil and ash, and subtracting from 100.

214. **Calcium.** Digest the residue from 212 in a mixture of 25 c.c. of concentrated hydrochloric acid and 5.c.c. of concentrated nitric acid on the hot plate for one-half hour, dilute, filter, and make up to 250 c.c. in a graduated flask. Any appreciable residue on the filter may indicate addition of barytes, silica, clay or alumina. Determine the calcium and magnesium in an aliquot portion of the solution by adding ammonia in small quantities until a precipitate is formed, then acetic acid in excess until redissolved, except for traces of iron which may be removed by filtration. Ammonium oxalate is added, and the calcium precipitate treated in the usual manner.

215. **Phosphoric acid.** Take an aliquot portion of

the solution prepared above, neutralize with ammonia, and clear with a few drops of nitric acid, add about 5 grams of dry ammonium nitrate or a solution containing that amount. To the hot solution add 50 c.c. of molybdic solution for every decigram of phosphoric acid that is present. Digest at about 65° for an hour, filter and wash with cold water, or preferably ammonium nitrate solution. Test the filtrate for phosphoric acid by renewed digestion and addition of more molybdic solution. Dissolve the precipitate on the filter with ammonia and hot water, and wash into a beaker to a bulk of not more than 100 c.c. Nearly neutralize with hydrochloric acid, and add magnesia mixture from a burette; add slowly (about 1 drop per second), stirring vigorously. After 15 minutes add 30 c.c. of ammonia solution of density 0.96. Let stand for some time; 2 hours is usually enough. Filter, wash with 2.5 per cent ammonia, ignite to whiteness or to a grayish white, and weigh as magnesium pyrophosphate.

216. Preparation of reagents. *Molybdic solution.* Dissolve 100 grams of molybdic acid in 400 grams or 417 cc., of ammonia, specific gravity 0.96, and pour the solution thus obtained into 1,500 grams or 1,250 c.c. of nitric acid, specific gravity 1.20. Keep the mixture in a warm place for several days, or until a portion heated to 40° deposits no yellow precipitate. Decant the solution from any sediment and preserve it in glass-stoppered vessels.

Magnesia Mixture. Dissolve 110 grams of crystallized magnesium chloride, 280 grams of ammonium chloride, in 700 c.c. of ammonia of specific gravity, 0.96, and sufficient water to make 2000 c.c.

217. Magnesium. The filtrate, from which the calcium has been precipitated, is evaporated to a small bulk and made alkaline with ammonia. After standing several, hours the magnesium precipitate is filtered, ignited, and weighed, and calculated to magnesium by multiplying by 21.88.

218. Calculations. The magnesium is calculated to magnesium phosphate, and the remainder of the phosphoric acid to calcium phosphate. Any calcium remaining is calculated to calcium carbonate.

Genuine ivory black, made by carbonizing waste fragments and turnings of ivory, is often adulterated with bone black, which is somewhat similar in composition, but contains only a small amount of magnesium phosphate as compared with the ivory black.

219. Specifications for drop black. (Navy Department, May, 1903). Drop black must be of good deep luster and consist of calcined bone black only. The addition of blue or gas carbon black will be ground for rejection. The paste must contain not less than 45 per cent of pure pigment.

The pigment must be of the best quality, free from all adulterants, and equal in all respects to the standard sample.

The paste must be ground in pure raw linseed oil only, to a medium stiff paste, which will break up readily in thinning.

220. Specifications for carbon black, etc. (Treasury Department, 1907). Carbon black must be pure gas carbon with not more than 0.5 per cent of ash, that is, 97.5 per cent of pure carbon and the balance moisture, ash, etc.

Hard black; should be suitable for making the highest class of plate printing inks; and other factors being equal, a color having chemical and physical properties adapted for that purpose and which produces an ink having the most satisfactory working qualities will be selected. The black now in use has the following chemical analysis:

	Per cent.
Ash	48.3
Moisture	3.7
Carbon	48.0

Ash insoluble in hydrochloric acid 11.4 per cent.

Soft Black. Requirements same as for hard black. The black in use has the following chemical analysis:

	Per cent.
Ash	56.1
Moisture	2.5
Carbon (by diff.)	41.4
	100.0

Ash insoluble in hydrochloric acid 36.3 per cent.

221. COMPOSITION OF IVORY AND BONE.

IVORY (*Uncalcined*).

	I. Per cent.	II. Per cent.
Calcium phosphate, including slight amount of calcium fluoride	38.48	46.48
Calcium carbonate	5.63	3.86
Magnesium phosphate	12.01	7.84
Soluble salts	0.70	0.77
Organic matter	43.18	41.05
	100.00	100.00

BONE (*Uncalcined*).

	I. Per cent.	II. Per cent.
Calcium phosphate	61.4	62.4
Calcium carbonate	8.6	7.9
Magnesium phosphate	1.7	1.7
Organic matter	28.3	28.0
	100.00	100.00

222. TYPICAL ANALYSES BY THE AUTHOR OF THE VARIOUS BLACKS.

	I. Ivory Drop Black Per cent.	II. Lamp Black Per cent.	III. Lamp Black Per cent.
Moisture	0.14	2.24	2.18
Oil	0.22	0.35	0.19
Ash	15.23	0.32	0.10
Carbon	84.41	97.09	97.53
	100.00	100.00	100.00

		I. Ivory Black[1] Per cent.		II. German Ivory Black Per cent.		III. Ivory Black[1] Per cent.
Moisture		0.75		2.33		2.59
Oil		0.17		0.22		0.14
Ash		88.98		84.82		84.70
Insoluble	0.88		0.42		0.32	
Calcium phosphate	73.72		77.51		77.82	
Calcium carbonate	14.00		6.51		5.60	
Magnesium phosphate	0.38		0.38		0.96	
Carbon		10.10		12.63		12.57
		100.00		100.00		100.00

Analysis of Mixed Paints Tinted with Black and Oxide of Iron Pigments.

223. Carbon. One gram of the pigment is dissolved in hydrochloric acid as described under white pigments, and the residue filtered through an ashless filter, that has been dried in the hot water oven and weighed. After washing the residue with boiling water the filter and contents are dried and weighed, then ignited until all the carbon is burned off, and weighed again. The percentage of carbon is obtained by difference. Where the percentage of color is small, it is often estimated by difference, adding together the determined constituents and subtracting from 100.

224. Ferric oxide. If the filtrate from the insoluble residue is of an appreciable yellow color it indicates that the tint has been "warmed up" by the addition of an ochre or oxide. In which case the lead is precipitated and estimated as described under analysis of white pigments, the filtrate from the lead sulphide heated until all of the hydrogen sulphide has been expelled and the iron

[1] Not true ivory blacks.

and alumina precipitated with ammonia after having been oxidized by boiling with a few drops of nitric acid, filtered and ignited and weighed in a porcelain crucible, the residue fused with bisulphate of potassium, dissolved in water with the aid of a little hydrochloric acid, heated to boiling, reduced with stannous chloride; mercuric chloride and manganous sulphate solution added and titrated with permanganate in the manner described under analysis of Venetian Reds.

225. **Alumina.** The alumina is calculated by difference from the data obtained under 224.

226. **Zinc oxide.** The filtrate from the iron and alumina precipitate and the filtrate from the lead sulphate precipitate, the alcohol having been removed by evaporation, are mixed, made distinctly alkaline with ammonia and the zinc precipitated with hydrogen sulphide. The liquid containing the zinc sulphide precipitate is heated to boiling, and about 5 grams of solid ammonium chloride added, which renders the precipitate easier to filter. Settle, filter, and wash thoroughly. Pierce filter, wash through into a clean beaker with water, dissolving the residue on filter with dilute hydrochloric acid and wash with hot water. Dilute, heat to expel hydrogen sulphide and titrate with ferrocyanide as previously described. If iron is absent in the paint the zinc may be estimated directly as described under analysis of white paints.

227. **Calcium and magnesium.** Estimate as usual in the filtrate from the zinc sulphide.

228. **Residue insoluble in hydrochloric acid.** Fuse with sodium carbonate as previously described. Dissolve in water and filter. Iron not previously dissolved will remain on the filter as ferric oxide along with any barium that may be present. This residue after thorough washing is dissolved with the aid of a small quantity of hydrochloric

acid, the barium precipitated as usual and the iron estimated in the filtrate from the barium sulphate. The silica and alumina are estimated as usual.

229. **Lead sulphate.** Determine the combined sulphuric acid as described under analysis of white paints and calculate to lead sulphate in the absence of calcium sulphate. If calcium carbonate and calcium sulphate are both present the nitric acid-alcohol separation should be used.

230. ANALYSES BY AUTHOR OF PAINTS TINTED WITH BLACKS, OCHRE AND IRON OXIDES.

	I. Light Drab.	II. Drab.
Net weight, lbs. and oz.	6:6	6:12
Capacity of can, qts.	2.06	2.03
Contents qts.	1.93	1.92

	Per cent.	Per cent.
Pigment by weight	56.6	56.9
Vehicle	43.4	43.1
	100.00	100.00

Analysis of Vehicle.

	Per cent.	Per cent.
Linseed oil	92.9	92.0
Turpentine drier	7.0	6.2
Water	0.1	1.8
	100.00	100.00

Analysis of Pigment.

		Per cent.		Per cent.
White lead		26.57		27.73
Lead sulphate		0.78		2.39
Zinc oxide		62.34		57.12
Color		10.31		12.76
Clay and silica	5.56		7.74	
Iron oxide	3.02		3.89	
Carbon and undetermined	1.73		1.13	
		100.00		100.00

Vandyke-Brown. Composition.

231. Vandyke-Browns vary widely in composition according to the method of preparation. Some are obtained from natural deposits of an organic nature, such as peat, decayed vegetable matter, etc.; or by the slight calcining of cork-cuttings, bark and twigs of trees; while some of the more common varieties are prepared by mixing lampblack or other black pigments with sufficient red oxide and ochre to give the desired shade.

232. Analyses of two Vandyke-Browns by the author gave the following results.

		I.		II.
Organic matter and moisture		90.95		91.10
Ash		9.05		8.90
Silica	1.90		2.61	
Alumina and ferric oxide	1.43		1.50	
Calcium carbonate	4.98		3.28	
Soluble salts	0.74		1.51	
		100.00		100.00

Analysis of Umbers and Siennas.

233. Hygroscopic moisture. Heat 2 grams at 105° C. for 3 hours. Loss in weight represents hygroscopic moisture.

234. Combined water. Transfer above sample to a weighed platinum crucible and heat for 1 hour over an ordinary lamp, or better in a muffle. Loss in weight indicates amount of combined water. Carbonates and organic matter render the results inaccurate. In which case continue the ignition at bright red heat for several hours, and weigh again. Determine the carbon dioxide in another portion of the sample and estimate the combined water by difference.

235. Silica and barium sulphate. One gram of the pigment is intimately mixed with 6 to 8 grams of potassium bisulphate and fused in a large porcelain crucible, the cover of which is small enough to set inside the top of the crucible, at not too high a temperature for one-half hour. Finally heating the side of the crucible to finish the conversion of any material adhering to the cover and upper portion of the crucible. The iron, manganese, aluminum, calcium, and magnesium are converted into sulphates, the barytes remains unchanged and the silica is completely dehydrated.

After cooling, the entire contents of the crucible may be shaken loose and dissolved in sufficient water and a little hydrochloric acid. Filter and make up to 250 c.c.

236. The residue remaining on the filter, which should be white, a red or brownish color indicating incomplete fusion with potassium bisulphate, in which case the sample must be fused again, is ignited and weighed in a platinum crucible. The residue is tested for barium sulphate by the flame test, if absent the residue is reported as silica; if present the residue is treated in the crucible with hydrofluoric acid until a thin paste is formed. The mixture is stirred with a platinum wire and digested at a gentle heat, finally two or three drops of sulphuric acid are added, and the temperature gradually raised until no further loss in weight takes place, indicating that the silica has been completely expelled. The residue is weighed as barium sulphate and the loss in weight represents the silica.

237. Ferric oxide. An aliquot portion of the solution from 235 is heated nearly to boiling and stannous chloride solution added cautiously until the yellow color has disappeared, and then a slight excess added. All at once with vigorous shaking of the flask 50 c.c. of mercuric chloride solution is added, then 50 c.c. of the manganous sulphate solution. Dilute with cold fresh boiled water and titrate with permanganate solution. Calculate iron found to ferric oxide.

238. **Manganese.** Digest 0.5 grams of the sample with 15 c.c. of concentrated hydrochloric acid until all of the iron and manganese has dissolved, then add 5 c.c. of sulphuric acid diluted with 10 c.c. of water, and evaporate on the hot plate until all of the hydrochloric acid is expelled as shown by copious evolution of sulphur trioxide fumes. Cool, dissolve in about 25 c.c. of water, and heat carefully with occasional shaking until all of the anhydrous sulphate of iron has dissolved. Transfer to a 250 c.c. graduated flask and add an excess of zinc oxide emulsion, obtained by mixing C. P. zinc oxide with water. Avoid a large excess, but sufficient to precipitate all the iron, so that on standing the solution begins to settle clear and some zinc oxide can be seen in the bottom of the flask. Cool and make up to the mark.

239. Transfer an aliquot portion to a beaker or flask, and add an excess of a saturated solution of bromine water and about 3 grams of sodium acetate. One c.c. of a saturated solution of bromine water will precipitate about 0.01 gram of manganese. Boil for about 2 minutes. Filter and wash with hot water. The filtrate must be perfectly clear. Place the filter containing the washed precipitate back in the beaker or flask in which the precipitation was made. All traces of bromine must be entirely expelled.

240. Add an excess of standard oxalic acid solution and about 50 c.c. of dilute sulphuric acid (1:9) and heat nearly to boiling with gentle agitation until the precipitate is entirely dissolved. Dilute to about 200 c.c. with hot water, and titrate with standard permanganate.

Standard oxalic acid solution. Dissolve 12.6048 grams of chemically pure oxalic acid in freshly boiled water and make to 1000 c.c. in a graduated flask.

One c.c. of this solution = .0055 gram of manganese. The oxalic acid solution should be standardized against the standard permanganate solution and the correction factor calculated.

Example: Wt. of sample taken = 0.5 gram.
Volume of solution = 250 c.c.
Aliquot portion used = 100 c.c. = 0.2 gram.
1 c.c. of permanganate sol. = 0.499 c.c. of oxalic acid.
1 c.c. of oxalic acid sol. = 0.0055 gram of manganese.

Permanganate solution used in titrating excess of oxalic acid solution = 13.2 c.c.

13.2 c.c. = 6.59 c.c. of oxalic acid.

Oxalic acid solution used,	10.00 c.c.
Excess,	6.59 c.c.
Consumed,	3.41 c.c.

$$3.41 \times .0055 = .018755 \text{ g Mn.}$$

$$\text{Mn} : \text{MnO}_2 : .018755 : x.$$

$$x = .02967 \text{ g. MnO}_2.$$

$$.02967 \div 0.2 = 14.84 \text{ per cent MnO}_2.$$

241. Alumina. Fifty c.c. of the 250 c.c. solution prepared in 235, is treated with about 20 grams of solid ammonium chloride, made just alkaline with ammonia, heated, allowed to settle, decanted, filtered and washed. The precipitate is dissolved on the filter with hydrochloric acid and after washing with small portions of boiling water, the iron and aluminum is reprecipitated, solid ammonium chloride being added as before. The precipitate is washed by decantation, filtered and the filtrate collected in the beaker containing the first filtrate. This treatment frees the iron and aluminum from any manganese and the precipitate may be dried, ignited and weighed in the usual manner, the alumina being obtained by difference. It is often advisable to make another reprecipitation of the iron and alumina, using but a small amount of ammonium chloride.

242. Calcium and magnesium. The combined filtrates from the iron and alumina are treated with colorless ammonium sulphide in such a manner as to form the green sulphide of manganese which is very much easier to filter than the pink sulphide.

The colorless ammonium sulphide may be prepared as follows: Saturate one-half of a solution of 100 c.c. of water and 50 c.c. of ammonia (sp. gr. 0.90) with hydrogen sulphide, and then add the other half of the solution.

For the precipitation of the manganese, 25 c.c. of the ammonium sulphide solution and 10 c.c. of ammonium chloride solution containing 3 grams of the dry salt, are placed in a 50 c.c. Erlenmeyer flask, the solution diluted to about 100 c.c. and heated. As soon as it comes to a boil, the combined filtrate from the iron and alumina is added and the beaker rinsed with a little water. The flask is shaken vigorously and the solution kept nearly at the boiling point. After alternate shaking and heating, the pink sulphide of manganese turns green and settles readily, leaving a clear supernatent liquid. If the ammonium sulphide is of the proper strength and a sufficient amount be used, there should be no difficulty in obtaining the green sulphide in proper condition for filtering.

After filtering off the manganese, the filtrate is evaporated to a syrupy consistency and 20 c.c. of nitric acid (sp. gr. 1.2,) added in small portions, evaporating each time. Sufficient hydrochloric acid is added and heat applied, until the brown fumes cease to be given off. This treatment which removes the excess of ammonium salts is not necessary if magnesium is known to be absent.

The solution after the removal of the nitric acid is diluted with water, made alkaline with ammonia and the calcium and magnesium, separated and estimated in the usual manner, both being calculated to the oxides.

The calcium may have been present as carbonate or sulphate or both. Hence an estimation of the combined sulphuric acid present in the original sample is necessary. For this purpose 1 gram is dissolved in 30 c.c. of strong hydrochloric boiled 10 minutes, diluted with 50 c.c. of water heated to boiling, filtered, and washed with hot water. Neutralize the filtrate with ammonia then make just distinctly acid with hydrochloric acid, boil, add 10 c.c. of barium chloride solution, continue boiling for 10 minutes, filter, wash, ignite and weigh as barium sulphate. Calculate combined sulphuric acid by multiplying weight of precipitate by 0.343.

Calculate the combined sulphuric acid found to calcium sulphate and the remaining calcium to oxide.

243. ANALYSES OF UMBERS AND SIENNAS BY THE AUTHOR.

	I. Raw Sienna.	II. Burnt Sienna.
Moisture	0.42	0.44
Loss on ignition	12.28	12.67
Silica	36.85	19.55
Ferric oxide	45.18	62.75
Alumina	3.00	1.66
Calcium oxide	1.09	2.52
Magnesium oxide	0.85	0.00
Sulphur trioxide	0.15	0.20
Manganese dioxide	0.13	0.17
Undetermined	0.05	0.04
	100.00	100.00

	III. Raw Umber	IV. Burnt Umber.
Moisture	1.78	2.01
Loss on ignition	13.64	3.94
Silica	20.60	24.21
Ferric oxide	42.60	51.04
Alumina	2.90	6.80
Calcium oxide	3.68	1.95
Magnesium oxide	2.16	...
Sulphur trioxide	0.36	0.22
Manganese dioxide	11.95	9.79
Undetermined	0.33	0.04
	100.00	100.00

Analysis of Mixed Paints Containing Umbers, Siennas and Ochres.

244. Determine the manganese in a separate sample as determined under the analysis of umbers. Determine the lead as in white paints, using the filtrate from the lead sulphide for the estimating of the iron, which must be oxidized by boiling with a little nitric acid before precipitating. Determine aluminum, zinc, calcium, and magnesium as described under analysis of umbers and siennas. The zinc being precipitated as the sulphide after the removal of the iron, and aluminum, is contaminated with manganese sulphide. Dissolve the mixed sulphides in dilute hydrochloric acid, boil until odor of hydrogen sulphide is expelled. Cool. Add excess of sodium hydroxide and filter off the precipitated manganese hydroxide, washing thoroughly. The filtrate containing the zinc in solution as sodium zincate, is acidified with hydrochloric acid, heated to about 80° C. and titrated with potassium ferrocyanide in the usual manner.

Any barytes, silica and insoluble silicates are separated and estimated as usual.

CHAPTER XIII.

ANALYSIS OF BLUE PIGMENTS AND PAINTS.

Analysis of Prussian Blues, Chinese Blues, etc.

245. **Hygroscopic moisture.** Heat 2 grams to 105° C. for 3 hours. Loss in weight represents hydroscopic moisture.

246. **Water of combination.** The water of combination, so called, cannot with advantage be determined directly, but can be approximated by subtracting the total per cent of constituents determined — hygroscopic moisture, cyanogen, iron, aluminum, alkali metal, alkaline sulphate and inert base, if any — from 100 per cent.

247. **Iron.** Ignite one gram at a temperature sufficient to decompose the last trace of the blue, but not so high as to render the oxide of iron difficult of solution. Dissolve in 25 c.c. of hydrochloric acid and 25 c.c. of water with aid of heat. Filter, making up filtrate to 250 c.c. Titrate 50 c.c. with potassium permanganate, after adding stannous chloride, mercuric chloride and manganous sulphate solution in the usual manner. Calculate to metallic iron.

248. **Aluminum.** Precipitate the iron and aluminum from 50 c.c. of the iron solution. Filter, ignite and weigh, estimating the alumina by difference. It probably exists in the Prussian blue as aluminum ferrocyanide. Calculate to metallic aluminum.

249. **Calcium.** Calcium compounds are very rarely found in Prussian blues. If the Prussian blue is precipitated on barytes, the latter is liable to contain a small

amount of calcium carbonate as an impurity. Treat the filtrate from 248 with ammonium oxalate. Settle, filter, ignite and weigh as calcium oxide. Calculate to calcium carbonate.

250. **Alkali metal and alkaline salts.** The filtrate from 249 is evaporated to dryness in a weighed evaporating dish, the ammonium salts completely volatized, the alkaline salts weighed, and the chlorine therein determined by titration with standard silver nitrate solution. The alkali metal, is, almost without exception, entirely sodium or potassium and not a mixture of the two, and may be identified by the flame test using a small fragment of the weighed alkaline salt. The sulphuric acid is estimated, in 50 c.c. of the solution prepared under 247, by precipitation with barium chloride, in the usual manner. The amount obtained is calculated to sodium sulphate or potassium sulphate as the case may be. The potassium or sodium chemically combined with the Prussian blue is calculated from the amount of chlorine found and reported as metallic sodium or potassium.

251. **Cyanogen.** Estimate the nitrogen in 1 gram of the sample by the Kjeldahl-Gunning method. Multiply the nitrogen obtained by 1.86 to convert it into cyanogen.

252. **Barytes, silica, clay, etc.** The insoluble portion remaining on the filter paper in 247 is ignited and weighed. Fuse with sodium carbonate and estimate the barytes, silica, alumina, etc., as described under analysis of white paints.

253. **Calculations.** The amount of Prussian blue may be calculated approximately by multiplying the iron content by 3.03 or the nitrogen content by 4.4. These factors are not exact as Prussian blues have varying compositions.

A Prussian blue to be considered pure should contain at least 20 per cent of nitrogen and 30 per cent of iron calculated on the dry matter and after burning should be entirely soluble in hydrochloric acid. A dry blue should contain less than 7 per cent moisture and the sulphuric acid in the Kjeldahl nitrogen determination should not be blackened which would indicate organic adulteration.

254. ANALYSES OF "PURE" PRUSSIAN BLUES.[1]

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Moisture (lost at 100° C.)	5.61	3.54	5.36	5.45	74.53	5.32	5.56	5.61
Water of combination, etc.	15.46	18.18	6.22	13.07	3.08	7.86	14.60	16.93
Cyanogen	37.72	41.10	42.97	37.90	10.64	39.91	40.19	40.86
Iron	29.48	32.16	34.27	30.32	7.97	30.94	31.94	31.25
Aluminum	1.82	.52	...	3.17	.72	1.00	1.43	1.52
Alkali metal (Na)	7.60	(K) 4.50	(K)7.72	(K)2.25	(K)1.06	(K)11.31	Na 2.52	.76
Alkaline sulphate	2.31	...	3.46	7.84	2.00	3.66	3.76	Na 3.07
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

255. ANALYSES OF CHINESE BLUES BY AUTHOR.

	I.	II.	III.
Moisture (lost at 100° C.)	2.49	3.45	2.04
Water of Combination, etc.	12.69	18.12	8.75
Cyanogen	45.78	36.51	46.09
Iron	35.87	32.34	35.86
Aluminum	...	...	...
Alkali metal	Na 1.57	(K)4.89	Na 3.80
Alkaline sulphate	1.50	3.61	3.35
Silica	0.10	1.08	0.11
	100.00	100.00	100.00

Analysis of Mixed Paints containing Prussian Blue, Chinese Blue, etc.

256. Weigh 1 gram into a 250 c.c. beaker, add 30 c.c. of concentrated hydrochloric acid, boil 5 minutes, add 50

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[1] Parry and Coste, The Analyst, Vol. XXI., page 227.

c.c. of hot water, boil 10 minutes, filter. Wash thoroughly with boiling water. Ignite, filter and precipitate gently, so as to destroy the blue color but not at a sufficiently high temperature to render the iron oxide difficultly soluble in acid. Cool digest in moderately concentrated hydrochloric acid until the iron is all dissolved. Dilute, filter, adding this filtrate to the first filtrate. The insoluble residue is ignited, weighed and fused with sodium carbonate, the barium, silica and alumina separated as described under analysis of white paints. The lead, iron, soluble aluminum, zinc and any calcium and magnesium compounds separated and estimated as described under analysis of mixed paints containing blacks and oxide of iron pigments.

257. If the paint in question is free from other iron pigments the percentage of Prussian blue may be calculated by multiplying the iron content by 3.03. If other iron pigments are present the nitrogen content must be determined; this multiplied by 4.4 will give the approximate amount of Prussian blue present.

Analysis of Ultramarine.

258. Properties. Ultramarine is a compound of silica containing alumina, soda, sulphur and combined sulphuric acid. It has been often stated that ultramarine cannot be mixed with white lead, because of the sulphur content of the ultramarine, but the author has ascertained that a great many paint manufacturers use it in tinting mixed paints where the percentage of white lead does not exceed that of the zinc, without any harmful results following. Ultramarines that are to be used in the manufacture of paper should be tested for their power of resisting the action of alum, by boiling 5 grams in a 5 per cent alum solution. As found on the market ultramarines vary much in tint, brilliance and coloring power.

259. **Moisture.** Heat 2 grams at 1.05° C. for 3 hours, cool and weigh.

260. **Silica.** Digest 1 gram in a casserole provided with a beaker cover, with 30 c.c. of concentrated hydrochloric acid. Evaporate to complete dryness, cool, add 2 c.c. of concentrated hydrochloric acid, evaporate to dryness, and heat gently for 15 minutes. Take up in 100 c.c. of hot water add 10 c.c. of hydrochloric acid. Filter, ignite and weigh as silica.

261. **Alumina.** The filtrate from the silica is made just sufficiently alkaline with ammonia to precipitate the aluminum, heat gently, filter, ignite and weigh as alumina.

262. **Sodium oxide.** The filtrate from the alumina is neutralized with sulphuric acid in a porcelain evaporating dish, evaporated to dryness, the residue treated with a little sulphuric acid, evaporated to dryness again, treated with water, evaporated to dryness, and ignited at low red heat, cooled and weighed.

Wt. sodium sulphate × 0.4366 = wt. of sodium oxide.

263. **Total sulphur.** Fuse 1 gram in a large crucible with a mixture of potassium nitrate and potassium chlorate for about half an hour. Dissolve the fused mass in dilute hydrochloric acid and boil the solution with strong nitric acid for half an hour, filter off the silica and precipitate the sulphuric acid with barium chloride in the usual manner. Filter, ignite, and weigh as barium sulphate.

From the weight of barium sulphate thus obtained deduct the weight found in 264, the difference is the amount due to sulphur present in the blue as sulphide.

Wt. barium sulphate × 0.1373 = wt. sulphur.

264. **Combined sulphuric acid.** Dissolve 1 gram in dilute hydrochloric acid. Filter off the silica, make filtrate

alkaline with ammonia and then just distinctly acid with hydrochloric acid and treat with barium chloride in the usual manner. The precipitated barium sulphate is filtered, ignited, and weighed as usual.

Wt. barium sulphate × 0.3434 = wt. of sulphur trioxide.

265. ANALYSES OF ULTRAMARINES BY THE AUTHOR.

	Ultramarine Blue. I.	Ultramarine Blue. II.	Ultramarine Blue. III.
Silica	39.26	39.45	41.92
Alumina	25.60	25.81	26.21
Sulphur	11.69	12.02	10.82
Sulphur trioxide	3.10	2.33	1.93
Sodium oxide	19.87	19.73	18.40
Water	0.48	0.66	0.72
	100.00	100.00	100.00

266 ANALYSES OF ULTRAMARINES BY HURST.

	Sulphate.	Soap Makers.	Calico Printers.	Paper Makers.
Silica	49.69	40.65	40.89	45.42
Alumina	23.00	25.05	24.11	21.15
Sulphur	9.23	12.95	13.74	11.62
Sulphur trioxide	2.46	4.81	3.05	5.58
Soda	12.49	14.26	15.61	9.91
Water	3.13	2.28	2.60	6.32
	100.00	100.00	100.00	100.00

Analysis of Cobalt Blue.

267. This pigment which is essentially a compound of the oxides of alumina and cobalt has largely gone out of use, but that it still finds a limited application is evidenced by the fact that the author receives occasional samples for analysis. Certain shades of ultramarine blue are often sold under the name of cobalt blue.

268. **Moisture.** Determine as usual.

269. Alumina. Fuse 1 gram with potassium bisulphate as described under analysis of Indian reds and Venetian reds. Dissolve in water and hydrochloric acid, filter and make up to 250 c.c. in a graduated flask. Any residue remaining on the filter paper is ignited and weighed as silica, unless barium sulphate is present which would be shown by the flame test.

An aliquot portion of the solution is treated with an excess of ammonium chloride, and then made just distinctly alkaline with ammonia. Filter, dissolve on the filter with hydrochloric acid and reprecipitate. Filter again, combining the two filtrates. Wash thoroughly, ignite and weigh as alumina.

270. Calcium and magnesium. The combined filtrates from the alumina are saturated with hydrogen sulphide, filtered and any calcium and magnesium estimated in the filtrate in the usual manner.

271. Cobalt oxides. The oxides of cobalt present are best estimated by difference, by substracting the determined constituents from 100. It is stated by Hurst that phosphoric acid is occasionally used in the manufacture of cobalt blues, in which case it should be removed before estimating the aluminum, calcium and magnesium. The several samples examined by the author were found to be free from phosphoric acid.

CHAPTER XIV.

ANALYSIS OF YELLOW, ORANGE, AND RED CHROME LEADS, ANALYSIS OF VERMILIONS.

272. **Composition.** The lemon yellow chromes usually contain sulphate of lead, sometimes carbonate of lead. The red chromes, known by the various names of scarlet chrome, chrome red, Chinese red, American vermilion, and vermilion substitute may be considered as basic chromates of lead. Often these basic chromes are brightened up by having precipitated on them an organic color; this may be tested for by treating a portion of the pigment with alcohol, which will dissolve the organic color, giving a strongly colored solution. See analysis of vermilions.

273. **Hygroscopic moisture.** Heat 2 grams at 105° C. for 3 hours. Loss in weight represents hygroscopic moisture.

274. **Barytes, silica and clay.** One gram of the pigment is boiled for 5 minutes with 30 c.c. of concentrated hydrochloric acid in a covered beaker. While boiling add half a dozen drops of alcohol one at a time. Fifty c.c. of water is added and the boiling continued for 10 or 15 minutes. Filter, wash thoroughly with boiling water, ignite and weigh. The insoluble residue is fused with sodium carbonate and the barium, silica and alumina separated as described under analysis of white paints.

275. **Lead.** The filtrate from the insoluble residue is neutralized with dilute ammonia until the further addition of another drop would cause the formation of a permanent

precipitate, diluted to about 250 c.c. to 300 c.c., and hydrogen sulphide passed in for 10 minutes.

Solutions containing large amounts of chromium if neutralized with ammonia until a permanent precipitate appears, seem to require an excess of hydrochloric acid for their resolution, sufficient to prevent the satisfactory precipitation of the lead with the hydrogen sulphide.

Allow the precipitate to settle thoroughly as it renders the filtering much easier, filter, wash with hydrogen sulphide water. Boil, filter, and precipitate with dilute nitric acid, until all of the lead has dissolved, filter with aid of suction, washing thoroughly with hot water. Add 5 c.c. of concentrated sulphuric acid, diluted with an equal volume of water to the filtrate. Evaporate on hot plate until the white fumes of sulphur trioxide appear. Cool, dilute with water, add an equal volume of alcohol, filter, washing with dilute alcohol, ignite gently, and weigh as lead sulphate. Save filtrate.

276. Chromium. The alcoholic filtrate from the lead sulphate is evaporated nearly to dryness to expel alcohol, and the filtrate from the lead sulphide heated until the hydrogen sulphide is expelled. The two filtrates are mixed, diluted if necessary, and made just perceptibly alkaline with ammonia; boil, settle, filter, wash thoroughly, ignite and weigh as chromic oxide.

Wt. chromic oxide × 1.3137 = wt. chromic anhydride.

Occasionally these pigments contain a small quantity of iron, which should be tested for qualitatively in a separate portion of the pigment. If found to be present the precipitate of ferric and chromium hydroxides is dissolved on the filter with hydrochloric acid, the filter washed thoroughly with hot water, and the iron and chromium in the filtrate reprecipitated with ammonia and treated with sodium peroxide to dissolve the chromium as described under the analysis of chrome greens.

277. **Calcium.** The filtrate from the chromium is treated with ammonium oxalate, allowed to stand in a warm place for an hour or so, filtered, washed thoroughly, strongly ignited and weighed as calcium oxide.

278. **Magnesium.** The magnesium is estimated in the filtrate from the calcium in the usual manner.

279. **Combined sulphuric acid.** The combined sulphuric acid may be estimated by either of the two methods given in paragraph 170, analysis of white paints. In fact, the latter method may be used for the rapid analysis of a chrome lead, the insoluble lead carbonate being filtered off, the chromium precipitated as the hydroxide in the usual manner, and the combined sulphuric acid estimated in the filtrate from the chromium.

Wt. barium sulphate × 0.3433 = combined sulphuric acid.

280. **Calculations.** If calcium is absent, or present as carbonate, the combined sulphuric acid is calculated to lead sulphate, the chromic anhydride to lead chromate, and excess of lead to lead oxide. If calcium sulphate and carbonate of lead are present, the carbon dioxide must be determined and the amount of calcium present as sulphate estimated by Thompson's method as described under analysis of white paints.

Wt. comb. sulphuric acid × 3.788 = wt. lead sulphate.

Wt. chromic anhydride × 3.230 = wt. lead chromate.

Wt. lead chromate × 0.6406 = wt. lead.

Wt. lead × 1.0773 = wt. lead oxide.

The specifications for chrome leads issued by the U. S. Treasury Department, 1907, state that a color containing lead sulphate is to be preferred to one containing white lead.

281. ANALYSES OF CHROME LEADS BY AUTHOR.

	Light Chrome Yellow.	Deep Orange Chrome Yellow.
Moisture	0.04	0.03
Lead chromate	68.65	40.56
Lead oxide	...	47.24
Lead sulphate	31.21	5.49
Silica	...	0.74
Alumina	...	0.44
Organic color	...	4.87
Undetermined	0.10	0.63
	100.00	100.00

Analysis of Mixed Paints Containing Chrome Yellows and Ochres.

282. **Barytes, silica and clay** are estimated as described under analysis of chrome leads.

283. **Lead,** both as sulphate and carbonate, is estimated as described under chrome leads, the filtrate from the lead sulphate being saved as before.

284. **Iron.** The filtrate from the lead sulphide is heated until all of the hydrogen sulphide has been expelled and added to the filtrate, from the lead sulphate, from which the alcohol has been expelled by boiling. A few drops of nitric acid are added and the solution boiled for a minute or two, then made just distinctly alkaline with ammonia, boiled, settled and filtered.

Dissolve on the filter with hot dilute hydrochloric acid, wash with hot water. *Cool.* Reprecipitate with ammonia, avoiding excess, without waiting for the precipitate to settle, carefully add a sufficient quantity of sodium peroxide (1 gram is usually sufficient) keeping the beaker covered meanwhile. Digest until all of the chromium and aluminum have passed into solution, adding more peroxide if necessary. The iron remains undissolved while the chromium and aluminum go into solution, filter, wash thoroughly, ignite strongly and weigh as ferric oxide, or dissolve in dilute hydrochloric acid and titrate. The treatment with peroxide is preferably performed in a porcelain evaporating dish.

285. **Chromium.** The filtrate from the iron is made up to 250 c.c. in a graduated flask. An aliquot portion is rendered acid with acetic acid and a slight excess of lead nitrate solution added, allowed to remain on the hot plate until thoroughly settled, filtered on to a weighed Gooch crucible, washed, dried and weighed as lead chromate.

286. **Aluminum.** An aliquot portion of the 250 c.c. solution is made just acid with hydrochloric acid, and then just distinctly alkaline with ammonia, allowed to settle, filtered on to a Gooch crucible, ignited and weighed as alumina.

287. **Zinc.** The filtrate from the chromium, iron and aluminum hydroxides, under iron is mixed with the filtrate from the lead sulphate from which the alcohol has been expelled, and the mixed solution saturated thoroughly with hydrogen sulphide, boiled with the addition of solid ammonium chloride to render the precipitate less slimy, and filtered. The zinc sulphide dissolved with hydrochloric acid, boiled to expel hydrogen sulphide and titrated with standard ferrocyanide of potassium as described under analysis of white paints.

288. **Calcium, magnesium and combined sulphuric acid** are estimated as described under analysis of Chrome Leads and the calculations made as there described.

Analysis of Vermilion.

289. **Properties.** Vermilion is a bluish scarlet powder, having a specific gravity of 8.2. It is insoluble in any single acid such as hydrochloric or nitric acid and in the alkalies. Heated in contact with the air it burns with a

pale blue lambent flame. Pure vermilion will burn away entirely or at least leave but a small fraction of 1 per cent of ash. This is a reliable test for it, as other adulterants would be left behind on heating.

The most common adulterants of vermilion are red lead, oxide of iron, lead chromes, vermilionette lakes, para reds, and alizarine reds.

290. Detection of vermilionettes, para and alizarine reds. (*a*). Boil a little of the dry color with water, settle and filter. Vermilionettes give a deep red solution, para reds a pale brownish or orange, and the alizarine reds a colorless solution.

(*b*). Boil a little of the dry color with a mixture of methyl and ethyl alcohol, filter, heat and settle. Vermilionettes give a bright red solution, usually having a yellow bloom, para reds an orange red solution, alizarine reds a practically colorless solution.

(*c*). Boil another portion of the dry pigment with some freshly distilled aniline, settle, and filter. Vermilionettes give a purple-red, alizarine lakes a pale brown, and the para reds an intense orange-red solution.

(*d*). Boil some of the dry color with a solution of caustic soda. Vermilionettes give a red solution with a green "bloom," para reds a bluish-red solution, while alizarine reds yield a characteristic deep violet solution.

291. Barytes, silica and clay. Dissolve 1 gram in 30 c.c. of concentrated hydrochloric acid, 50 c.c. of water with the aid of 1 to 2 grams of potassium chlorate added in small portions and warming. Evaporate to dryness on water-bath. Take up in 50 c.c. of water acidulated with hydrochloric acid, heat to boiling to dissolve any lead chloride, filter, wash with boiling water, ignite and weigh any insoluble residue. Fuse with sodium carbonate and estimate the barium sulphate, silica and alumina as described under analysis of white paints.

292. **Lead.** If lead is present, calcium compounds being absent, the filtrate is treated with sulphuric acid, evaporated carefully to expel excess of hydrochloric acid, diluted with water and alcohol, the lead sulphate filtered off on a Gooch crucible in the usual manner.

293. **Mercuric sulphide (vermilion).** The filtrate from the insoluble residue, if lead is absent, or the filtrate from the lead sulphate, is heated with a little sulphurous acid to reduce any iron present to the ferrous condition, made neutral with ammonia, and then *just* acid to litmus with hydrochloric acid.

The solution is diluted to about 350 c.c. and hydrogen sulphide passed in for 10 minutes. The mercuric sulphide is filtered off on a weighed Gooch crucible, washed with hydrogen sulphide water, the crucible removed to another holder and washed with alcohol and carbon bisulphide to remove sulphur, dried in steam-oven and weighed.

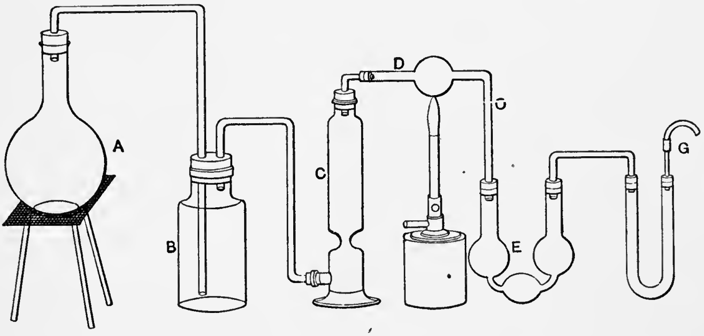

Fig. 11.

294. **Estimation of lead and mercury, calcium compounds present.** The filtrate from the insoluble residue from 291 is precipitated with hydrogen sulphide as de-

scribed under 293, collected on a weighed filter and dried at 100° C., weighed and mixed uniformly.

An aliquot part is introduced into the bulb of Fig. 11. A slow stream of washed chlorine gas passed through it, and a gentle heat applied to the bulb, increasing this gradually to faint redness. The escaping chlorine is conducted into a flue. First, sulphur chloride distils over, which decomposes with the water in *E* and *F*. The mercuric chloride formed volatilizes, condensing partly in *E*, partly in *O*. Cut off that part of the tube, rinse the mercuric chloride into *E* and mix the contents of the latter with the water in *F*. Mix the solution with excess of ammonia and warm gently until no more nitrogen is evolved, acidify with hydrochloric acid, filter and determine the mercury in the filtrate as under 293.

295. Ferric oxide. The filtrate from the sulphides is heated until all of the hydrogen sulphide has been expelled and the iron chromium and alumina precipitated with ammonia, filtered and separated as described under analysis of chrome greens.

296. Zinc oxide. The filtrate from the iron and alumina precipitate is made distinctly alkaline with ammonia and the zinc precipitated with hydrogen sulphide. The liquid containing the zinc sulphide precipitate is heated to boiling, and about 5 grams of solid ammonium chloride added, which renders the precipitate easier to filter. Settle filter, wash thoroughly. Pierce filter, wash through into a clean beaker with water, dissolving the residue on filter with dilute hydrochloric acid, and washing with hot water. Dilute, heat to expel hydrogen sulphide and titrate with ferrocyanide as previously described. If iron is absent in the paint, the zinc may be estimated directly as described under analysis of white pigments.

297. Calcium and magnesium. Estimated as usual in the filtrate from the zinc sulphide.

298. Calculations. If chromium is present it is calculated to basic lead chromate, and any excess of lead above that required to form the chromate is calculated to red lead.

299. ANALYSES OF VERMILIONS BY THE AUTHOR.

	I. English Vermilion Deep.	II. English Vermilion. Pale.	III. Vermilion.
Sulphide of Mercury	99.53	99.61	99.61
Ash.	0.47	0.39	0.39
	100.00	100.00	100.00

	I. Vermilion.	II. Radium Vermilion.
Moisture	0.16	0.06
Red lead	80.08	97.99
Barytes	16.83	. . .
Alumina	0.77	. . .
Organic color	2.16	1.95
	100.00	100.00

	I. Light Vermilion.	II. Deep Vermilion.
Moisture	1.33	0.15
Lead chromate	50.16	53.60
Lead oxide	41.20	40.88
Lead sulphate	6.15	4.97
Ferric oxide	0.37	0.33
Soluble salts	0.33	trace
Undetermined	0.46	0.07
	100.00	100.00

300. Antimony vermilion and orange. These two pigments have the same composition, corresponding to the formula of antimony trisulphide. They are insoluble in dilute acids, but soluble in strong hydrochloric acid. It is seldom necessary to make a complete analysis of these pigments. Adulteration will be indicated by the pigment not being completely soluble in strong hydrochloric, though a trace of sulphur may remain undissolved, floating on top of the acid.

300a. Analysis of Red Lead.[1] Solutions required: $\frac{n}{10}$ iodine solution, stannous chloride solution (14.1 g. in 1000 c.c.), starch paste solution. Pipette 25 c.c. of the stannous chloride solution into an Erlenmeyer flask, add 40 c.c. hydrochloric acid, boil one minute, add 100 c.c. cold water, cool rapidly and titrate with the iodine solution, using starch paste as an indicator.

Weigh 1 gram of the sample red lead into a similar Erlenmeyer flask, moisten with water, add 25 c.c. stannous chloride and 40 c.c. of hydrochloric acid, boil until all of the lead is in solution, and titrate with iodine solution as above. The difference in c.c. of iodine solution used in the blank and in the determination give the number of c.c. of iodine solution to which the available oxygen in the red lead is equivalent.

$$1 \text{ c.c. } \frac{n}{10} \text{ iodine sol.} = 0.8 \text{ m.g. oxygen.}$$

$$\text{Available oxygen} \times 42.73 = \text{amount of red lead.}$$

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[1] J. H. Wainwright, Engineering Chemistry.

CHAPTER XV.

ANALYSIS OF CHROME GREENS AND EMERALD GREENS.

Analysis of Chrome Greens.

301. Hygroscopic moisture. Heat 2 grams of the sample at 105° C. for 3 hours. Cool and weigh.

302. Organic color. Occasionally chrome greens are brightened up by treatment with an organic color. Boil a portion of the sample with alcohol; a green colored solution not due to suspended particles indicates the addition of an organic color.

303. Barytes, silica, clay, or other silicates. Weigh 1 gram into a porcelain crucible, heat gently, so as to destroy the Prussian blue, but not at a temperature sufficiently high to fuse the lead chromate or render the iron difficultly soluble in acid. Cool. Boil gently with 30 c.c. of concentrated hydrochloric acid in a covered beaker until all of the iron and lead have gone into solution. A few drops of alcohol added one at a time may assist the solution. Add 50 c.c. water; boil for 15 minutes. Filter hot, wash thoroughly with boiling water, ignite and weigh. Fuse with sodium carbonate and estimate the barytes, silica and alumina as described under analysis of white paints.

304. Lead. The filtrate from the barytes, silica and alumina is made just alkaline with ammonia, and then just acid to litmus, with hydrochloric acid; dilute to about 300 c.c. and pass in a current of hydrogen sulphide for 10 minutes. Allow the precipitate to settle *thoroughly.*

Filter, wash with hydrogen sulphide water. Digest precipitate and filter in a covered beaker with dilute nitric acid until the lead is entirely dissolved, filter on suction funnel, wash with hot water. Add 5 c.c. of concentrated sulphuric acid diluted with an equal volume of water to the filtrate; evaporate on sand bath until white fumes of sulphur trioxide appear. Cool, dilute with 50 c.c. of water, add 75 c.c. of alcohol and allow to stand for upwards of an hour with occasional stirring. Filter on to Gooch crucible, washing with water containing 2 per cent sulphuric acid, finishing with 50 per cent alcohol; dry, heat gently, and weigh as lead sulphate. Reserve, filtrate.

305. **Iron.** The filtrate from the lead sulphide is heated to expel the hydrogen sulphide and added to the filtrate from the lead sulphate, which has been boiled until all of the alcohol has been expelled. A few drops of nitric acid are added, the solution boiled for a minute or two and then made just distinctly alkaline with ammonia, filtered and washed. Dissolve on the filter with hot dilute hydrochloric acid, wash with hot water, *cool.* Reprecipitate with ammonia, avoiding excess, without waiting for the precipitate to settle; carefully add a sufficient quantity of sodium peroxide (1 gram is usually sufficient) keeping the beaker covered meanwhile. Digest until all of the chromium and aluminium have passed into solution, adding more peroxide if necessary. The ferric hydroxide remains undissolved and is filtered off, washed thoroughly, ignited, and weighed as ferric oxide.

306. **Chromium.** The filtrate from the ferric hydroxide is made up to 250 c.c. in a graduated flask, and an aliquot portion is rendered acid with acetic acid, a slight excess of lead nitrate added, and heated on the hot plate until the precipitate has thoroughly settled. Filter on to a weighed Gooch crucible, dry, and weigh as lead chromate,

or, the precipitate may be heated gently over an ordinary flame, so as not to fuse the chromate.

307. **Aluminium.** An aliquot portion of the 250 c.c. solution is made just acid with hydrochloric acid, and then just distinctly alkaline with ammonia. The precipitate of aluminium hydroxide allowed to settle, filtered, ignited and weighed as alumina.

308. **Calcium and magnesium** are estimated in the filtrate from the iron, aluminium and chromium hydroxides as usual.

309. **Cyanogen.** One gram of the sample is digested with sulphuric acid and the nitrogen estimated as under analysis of Prussian blues.

Wt. nitrogen × 1.86 = wt. Cyanogen.

310. **Combined sulphuric acid.** Heat gently 1 gram of the pigment so as to destroy the Prussian blue, dissolve in 30 c.c. of strong hydrochloric acid in a covered beaker. Dilute with 50 c.c. boiling water, boil 5 minutes, filter, make filtrate neutral with ammonia, then slightly acid with hydrochloric acid, bring to boiling, add 15 c.c. barium chloride, boil 10 minutes, filter, wash with hot water, ignite, and weigh.

Wt. barium sulphate × 0.3433 = combined sulphuric acid.

311. **Calculations.** The amount of Prussian blue present may be calculated, either by multiplying the iron content by 3.03 or the nitrogen content by 4.4. The chromium is calculated to lead chromate and the combined sulphuric acid, in the absence of calcium sulphate, to lead sulphate excess of lead over that required for the lead chromate and lead sulphate, calculated to lead oxide, unless the basic carbonate of lead were present, which is very rarely the case.

NOTE. In making an analysis of a mixed paint tinted with a green, it should be borne in mind that the Prussian blue is occasionally replaced with an ultramarine blue.

312. ANALYSES OF CHROME GREENS BY THE AUTHOR.

	I. Light Chrome Green.	II. Medium Chrome. Green.
Moisture	0.20	0.10
Lead chromate	16.57	16.67
Lead sulphate	5.80	5.29
Prussian blue	5.98	6.80
Barytes	68.22	66.72
Alumina	1.40	1.94
Silica	1.71	1.66
Undetermined	0.12	0.82
	100.00	100.00

Emerald Green, Paris Green and Arsenic Insecticides.

313. **Properties.** The chief use of emerald green, better known as Paris green, is as an insecticide, but little being used as a paint pigment owing to its poisonous qualities. As a pigment it is very opaque, has good covering power and is fairly permanent. It is completely soluble in ammonia, turning it to an intense blue color. This test, however, is not conclusive, since white arsenic and a number of other substances used in adulterating Paris green are soluble in ammonia and would escape detection if this method alone were depended on.

Under the terms of the North Dakota law regulating the sale of Paris green it shall be deemed adulterated if it contains less than 50 per cent of total arsenious oxide, or more than 4 per cent of free or uncombined arsenious oxide. In most cases the determination of water soluble and total arsenious oxides is sufficient.

314. **Water soluble arsenious oxide.** One-half gram of the sample is weighed into a 250 c.c. Erlenmeyer flask,

100 c.c. of distilled water added. The flask is agitated by shaking every few minutes during a working period of 8 hours, keeping the temperature between 25° to 30° C. The next day, after pouring off the clear liquid, 100 c.c. of distilled water is again added, and the shaking treatment repeated. The clear solution is again poured off, and the operation repeated with a fresh portion of 100 c.c. of distilled water. The three 100 c.c. leachings are combined and filtered through a double filter and titrated with tenth-normal iodine, using starch as an indicator as follows:

Add 20 c.c. of a saturated solution of sodium bicarbonate to every 0.1 gram of arsenious oxide and titrate as usual.

1 c.c. tenth-normal iodine = 0.00495 arsenious oxide.

315. **Total arsenious oxide.** Weigh 1 gram of the sample into a side-neck distilling flask, and add 5 grams of ferrous sulphate. Connect with a condenser, the other end of which dips below the surface of about 100 c.c. of distilled water, which is kept cooled. Fifty c.c. of hydrochloric acid are added to the flask containing the sample, which also has a glass tube leading nearly to the bottom, the other end of which is connected with a flask, in which hydrochloric acid gas is generated. This gas is very readily obtained by allowing concentrated sulphuric acid to drop into concentrated hydrochloric acid saturated with sodium chloride. The flask containing the arsenic solution is cooled nearly to zero, by immersing the flask into a vessel containing cracked ice. Pass in the hydrochloric acid gas; when no more is absorbed, the ice is removed and the solution brought to a boil. The stream of hydrochloric acid gas is allowed to flow and the distillation continued until the volume of the solution is reduced to about 25 c.c. The distillate is just neutralized with a

solution of sodium hydroxide or sodium carbonate, a sufficient amount of sodium bicarbonate added, the whole solution made to a definite volume and an aliquot part titrated with tenth-normal iodine and starch.

316. ANALYSES OF PARIS GREENS, BY E. F. LADD.

Laboratory Number.	Free Arsenious Oxide.	Total Arsenious Oxide.
101	3.46	52.38
102	7.41	54.36
103	1.73	45.46
104	6.17	57.32
105	1.98	57.32
106	1.48	56.34
107	7.41	59.72
108	18.77	51.39
109	5.93	52.18
110	.98	50.01
111	3.70	...

An inspection of the above shows that five of the samples contained excessive amounts of free arsenious oxide ranging from 9.93 to 18.77 per cent, while one of the samples contained a total of 45.46 per cent of arsenious oxide instead of 50 per cent prescribed as a minimum.

If a complete analysis is desired, the following scheme may be used.

317. Moisture. Heat 2 grams at 105° C. for 2 hours, cool and weigh.

318. Aniline color. Treat a portion of the sample with alcohol, after settling. If the solution remains distinctly green, an aniline color is present.

319. Insoluble residue. Digest 1 gram with dilute nitric acid, filter and wash with hot water. Residue may consist of lead sulphate, barium sulphate, silica, and clay. Digest residue with a strong solution of acid ammonium acetate in order to dissolve the lead sulphate; filter, wash with hot water. To the filtrate add dilute sulphuric acid, evaporate nearly to dryness. Cool and take up with water, filter on Gooch crucible, wash with 50 per cent alcohol, ignite, and weigh as lead sulphate. The residue from the ammonium acetate treatment is fused with sodium carbonate, and the barium, alumina and silica separated as usual.

320. **Lead chromate.** The nitric acid filtrate is treated with 1 c.c. of sulphuric acid, evaporated nearly to dryness, cooled, taken up with water, any lead sulphate present filtered off and calculated to lead chromate.

321. **Copper.** Dilute the filtrate from the lead sulphate to about 200–250 c.c. Pass hydrogen sulphide through the liquid for half an hour, maintaining the temperature at 70° C. Settle, filter, wash with hydrogen sulphide water. Transfer filter and contents to a 250 c.c. beaker, add excess of strong solution of sodium sulphide, digest for 30 minutes at a gentle heat. Filter. The residue which consists of copper sulphide is dissolved in dilute nitric acid freed from sulphur by filtration, and the copper determined electrolytically or by the iodide method. Calculate to cupric oxide.

322. **Arsenic.** The arsenic is best determined as described above under the estimation of total arsenious oxide.

323. **Chromium and zinc.** The filtrate from the copper and arsenic sulphides is boiled to thoroughly expel the hydrogen sulphide, ammonia added until alkaline. A greenish precipitate indicates chromium, a white precipitate, zinc hydroxide. In the latter case add sufficient ammonia to redissolve the zinc. Heat, filter, ignite and weigh as chromium oxide. The filtrate from the chromium, or the solution if chromium was absent. is saturated

with hydrogen sulphide to precipitate the zinc as sulphide, boil, adding 5 grams of solid ammonium chloride to render the precipitate less slimy. Dissolve in hydrochloric acid and titrate with standard potassium ferrocyanide as described under analysis of white pigments.

324. **Calcium.** The filtrate from the zinc is boiled to expel hydrogen sulphide made more strongly alkaline with ammonia, and the calcium precipitated with ammonium oxalate and estimated as usual. A determination of sulphates should be made so as to ascertain whether the calcium was present as carbonate or sulphate.

325. **Magnesium.** If a considerable quantity of calcium is present the filtrate from the calcium is tested for magnesium, which if found is estimated as usual.

326. **Acetic acid.** The acetic acid may be obtained by difference, or if desired estimated by C. Mohr's process as described in Sutton's Volumetric Analysis.

327. ANALYSES OF A PARIS GREEN BY HURST.

Water	0.90
Copper oxide	32.55
Arsenious acid	57.31
Acetic anhydride	6.63
Sulphur trioxide	1 67
Undetermined	0.94
	100.00

CHAPTER XVI.

EXERCISES IN COLOR MAKING.

328. The following formulas for the preparation of the more common colors are intended only for the analyst who may wish to acquire a little insight into the principles underlying the manufacture of colors by making a few experiments for himself. The formulas used by color makers are kept as secret as possible, and probably each manipulator has his own modifications which enable him to manufacture colors of greater strength and permanence to light than any novice may hope to do in a set of beakers in the laboratory.

329. Para-nitroaniline lake. Seven grams of para-nitroaniline is added to 15 grams of pure concentrated hydrochloric acid and 200 c.c. of water. Heat until all of the para-nitroaniline is dissolved. Cool to below 40° F. and then *slowly* and with *constant stirring* add 5 grams of sodium nitrite dissolved in 20 c.c. of water, keeping the solution cool with ice. Allow to stand one-half hour. Then add 15 grams of sodium acetate dissolved in 100 c.c. of water and 100 grams of inert base, like blanc fixé, which has been thoroughly freed from lumps.

In the meanwhile 7 grams of beta-naphthol are dissolved in 3 grams of sodium hydroxide and 175 c.c. of boiling water. Cool to below 45° F. and then add slowly and with constant stirring to the preparation of para-nitroaniline, keeping the particles of blanc fixé in thorough suspension. The lake forms at once. Wash by decantation, filter, and dry at a low temperature.

If a bluer shade is desired use beta-naphthol R.

330. Crimson red lake. For the preparation of this lake use 7 grams of alphanapthylamine instead of the para-nitroaniline, and conduct the process exactly as described under the manufacture of para-nitroaniline lake, using the same ingredients and the same amounts.

331. Emerald green. Dissolve 25 grams of copper sulphate in 200 c.c. of water; add 7 grams sodium crystals or 3.5 grams of the dry carbonate. This will precipitate part of the copper as copper carbonate. Then add just sufficient acetic acid to dissolve the copper carbonate.

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In a separate beaker dissolve 15 grams of arsenious acid and 22 grams of soda crystals, or 9.5 grams of dry carbonate, in 150 c.c. of water. Heat both solutions to boiling and pour the arsenic solution slowly and evenly into the copper solution with constant stirring. Wash by decantation, filter and dry.

332. Pale lemon chrome. 1. Lead solution. Lead acetate 50 grams in 150 c.c. of water.

2. Bichromate solution. Dissolve 8 grams of sodium bichromate in 100 c.c. of water.

3. Sulphuric acid. Dilute 8 grams of sulphuric acid with 25 c.c. of water.

Add the diluted sulphuric acid to the sodium bichromate solution and run the mixture slowly from a separating funnel into the lead acetate solution, with constant stirring. Settle, wash by decantation 4 times, filter, dry and grind.

333. Medium chrome yellow. 1. Lead solution. Dissolve 50 grams lead acetate in 125 c.c. of water.

2. Bichromate solution. Dissolve 9 grams of sodium bichromate in 75 c.c. of water.

3. Sulphuric acid. Dilute 6 grams of sulphuric acid with 25 c.c. of water. Precipitate and treat as described under pale lemon chrome.

Interesting results may be obtained by experimenting with an excess of each ingredient, precipitating at different temperatures and with different concentrations.

334. **American vermilion—basic lead chromate.** 1. Lead solution. Dissolve 50 grams of lead nitrate in 150 c.c. of water.

2. Bichromate solution. Dissolve 17 grams of powdered sodium bichromate in 100 c.c. of water.

3. Slaked lime. Carefully slake 6 grams of fresh lime; reduce to a thin paste in a mortar until free from lumpy particles.

Place the bichromate solution in a separating funnel and allow to run slowly into the lead nitrate with constant stirring. Settle, pour off the supernatent liquid. Add the lime and heat to boiling, with constant stirring, until the required shade has fully developed. Settle, wash four times by decantation, filter, dry and grind.

335. CHINESE BLUE. NUMBER I.

	Grams.
Potassium ferrocyanide	25
Ferrous sulphate	25
Potassium bichromate	2
Sulphuric acid	12
Potash alum	3

Dissolve the ferrous sulphate and alum in 200 c.c. of water. Dissolve the ferrocyanide in 200 c.c. of water and run the iron solution into it with constant stirring. Run in the dichromate dissolved in 25 c.c. of water, and then add the acid with constant stirring. Settle, wash by decantation three times, filter and dry.

336. CHINESE BLUE. NUMBER II

	Grams.
Potassium ferrocyanide	25
Ferrous sulphate	25
Chloride lime	5
Sulphuric acid	3
Hydrochloric	½

Dissolve and mix the ferrous sulphate and ferrocyanide as described above. Settle. Draw off the supernatent liquid, and add the chloride of lime, dissolved in 75 c.c. of water, through a fine sieve. Finally add the sulphuric acid, stir, settle, decant three times, filter and dry.

337. CHINESE BLUE. NUMBER III.

	Grams.
Potassium ferrocyanide	25
Ferrous sulphate	26
Potassium chlorate	4
Sulphuric acid	29

Prepare as described under Chinese Blue. Number I.

338. Brunswick greens. These greens are prepared by precipitating the yellow first, usually on an inert base like barytes, and then precipitating the blue over the yellow.

Pale green. Precipitate 35 grams of chrome yellow on 100 grams of barytes, and precipitate 1.5 grams of Prussian blue on the yellow, with vigorous stirring in each case.

Medium green. 35 grams chrome yellow, 100 grams barytes and 2.5 grams of Prussian blue.

Deep green. 35 grams of chrome yellow, 100 grams of barytes and 5 grams of Prussian blue.

CHAPTER XVII.

ANALYSIS OF JAPANS AND DRIERS.

339. At the present time the terms "Japan" and "drier" are interchangeable and refer to the same line of products, — manganese linoleate, lead lineolate, resinate of manganese, resinate of lead, or mixtures of these compounds. Originally Japan contained a considerable quantity of dissolved resin, constituting a preparation that on drying gave a film of considerable hardness and lustre, but this distinction has largely disappeared. These compounds should not be confused with baking Japans, which represent an entirely different class of products and which will not be discussed at this time. Japans and driers are usually made by heating the oxides of lead and manganese or borate of manganese with linseed oil or the various resins, and dissolving the melted mass in turpentine, benzine or mixtures of both.

340. Determination of the drying salts. The salts generally used are

	Litharge,	PbO
	Red lead,	Pb_3O_3
	Oxide of manganese,	MnO_2
	Borate of manganese,	MnB_2O_4
occasionally	Zinc sulphate,	$ZnSO_4$,
and	Zinc oxide,	ZnO.

Weigh 25 grams of the drier into a 250 c.c. Erlenmeyer flask and dilute with 25 c.c. of a mixture of equal parts of benzine and turpentine. Add 50 c.c. of dilute hydrochloric acid (1.10 sp. gr.) Allow to stand 1 hour, shaking thoroughly at intervals of 10 minutes. Immerse the flask in a beaker of hot water, at a considerable distance from the flame. When the contents of the flask are hot, shake with a circular motion, avoiding undue pressure in the flask. Allow to stand until cool, so as to be sure that the drier has been wholly dissolved. Pour into a separatory funnel, draw off the aqueous layer into a casserole, wash the oil portion twice with warm water, adding the washings to the casserole and evaporate to dryness under the hood. Dissolve in dilute nitric acid with the aid of heat, filter into a 250 c.c. graduated flask and after washing thoroughly make up to the mark.

341. **Lead.** To an aliquot portion add 5 c.c. of dilute sulphuric acid and evaporate on the hot plate until white fumes of sulphur trioxide appear. Cool, add cautiously 50 c.c. of water, heat to boiling, cool slightly, and add 50 c.c. of alcohol. Allow to stand one-half hour, filter on to a Gooch crucible, wash with 50 per cent alcohol, dry, heat gently and weigh as lead sulphate.

342. **Manganese.** To an aliquot portion of the sample add 5 c.c. of sulphuric acid dilute with 10 c.c. of water, and evaporate on the hot plate until all of the hydrochloric acid is expelled as shown by copious evolution of sulphur trioxide fumes. Cool, dissolve in about 25 c.c. of water and heat carefully with occasional shaking until all of the anhydrous sulphate of iron has dissolved. Transfer to a 250 c.c. graduated flask and add an excess of zinc oxide emulsion, obtained by mixing C. P. zinc oxide with water. Avoid a large excess, but sufficient to precipitate all the iron, so that on standing the solution begins to settle clear and some zinc oxide can be seen in the bottom of the flask. Cool and make up to the mark. Transfer an aliquot portion to a beaker or flask and add an excess of a

saturated solution of bromine water, and about 3 grams of sodium acetate. One c.c. of a saturated solution of bromine water will precipitate about 0.01 gram of manganese. Boil about 2 minutes. Filter and wash with hot water. The filtrate must be perfectly clear. Place the filter containing the washed precipitate back in the beaker or flask in which the precipitation was made. All traces of bromine must be entirely expelled.

Add an excess of standard oxalic acid solution and about 50 c.c. of dilute sulphuric acid (1:9) and heat nearly to boiling with gentle agitation until the precipitate is entirely dissolved. Dilute to about 200 c.c. with hot water and titrate with standard permanganate.

343. **Zinc.** Zinc sulphate and zinc oxide are but little used at present in driers. If present zinc may be estimated in the filtrate from the lead sulphate, as described under the analysis of mixed paints containing umbers and siennas.

344. **Calculations.** The color of the drier gives a clue as to the combinations used, borate of manganese being used in light colored driers, oxide of manganese in dark driers, and the oxides of lead in medium colored driers. By far the most common combination is a mixture of borate of manganese and litharge.

345. **Determination of the volatile oils.** Five grams of the drier is quickly weighed into a flat-bottomed dish, a petri-plate is the most suitable, dried for 3 hours at 150° C., cooled and weighed. Loss in weight represents very closely the amount of volatile thinner present, and in the samples analyzed by the author the volatile thinners constituted 63 to 68 per cent by weight.

346. **Separation of benzine and turpentine.** About 100 grams of the drier is distilled to the point of incipient decomposition, the distillate redistilled and the benzine

estimated by the Sulphuric Acid Number, as described under the analysis of volatile oils, Chapter IV.

347. **Detection of rosin.** About 1. c.c. of the drier is dissolved in 15 c.c. of acetic anhydride, warming until the solution is complete. Cool, filter, place a few drops of the filtrate on a crucible cover and add a drop of sulphuric acid, so that it will mix slowly. If rosin is present a characteristic fugitive violet color results. Lineolate driers sometimes give a color resembling that of rosin driers, and it is better to evaporate a portion of the drier to a syrup consistency, treat with alcohol, and test the alcoholic extract.

348. **Practical tests.** The chemical analysis of a Japan will give very little information regarding its efficiency, since the latter is largely dependent upon the conditions of manufacture. The following specifications,[1] as adopted and used by the Philadelphia and Reading Railroad, give very excellent methods for determining the efficiency of a Japan.

"The material desired consists of a pure turpentine hardener and oil drier, conforming to the following:

1st. When equal parts by weight of the Japan and of pure turpentine are thoroughly mixed and poured over a slab of glass, which is then placed nearly vertical at a temperature of 100° Fahrenheit, with a free access of air, but not exposed to draught, the coating shall be hard and dry, neither brittle nor sticky, in not exceeding 12 minutes.

2d. When thoroughly mixed with pure raw linseed oil at the ordinary temperature in proportions of 5 per cent, by weight of Japan to 95 per cent by weight of raw linseed oil, no curdling shall result, nor any marked separation or settling on standing.

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[1] Practical Testing and Valuation of Japan, by Robert Job, Chemical Engineer, Vol. IV., No. 5.

3d. When the above mixture is flowed over a slab of glass, which is then placed nearly vertical, at a temperature of 100° Fahrenheit, with free access to air, but not exposed to draught, the coating shall dry throughout, neither brittle nor sticky, in not exceeding 2 hours.

4th. When five cubic centimetres of the Japan are poured into 95 cubic centimetres of pure turpentine at the ordinary temperature, and thoroughly shaken, a clear solution shall result, without residue, on standing 1 hour.

5th. After evaporation of the turpentine, the solid residue must be hard and tough, and must not 'dust' when scratched with a knife.

6th. Benzine or mineral oil of any kind will not be permitted.

Shipments which are not closely in accordance with these specifications, or which are not of uniform quality throughout, will be returned at the expense of the shipper."

349. The temperature of 100° F. is obtained by the use of a suitable oven. The strips of glass used being 4 inches long by 2 inches wide. They are so placed in the oven that there is free access of air, but no draught. The bulb of the thermometer is placed beside the glass strips and the dryness of the film tested opposite the bulb of the thermometer.

The addition of rosin renders the dry film brittle and hence will "dust" when scratched with a knife.

The majority of driers used for house and barn paints are weak driers, and will not meet the above requirements. However, if the chemist will test out a few high-class driers by the above specifications, he will have but little trouble in estimating the value of the cheaper and inferior driers.

The United States Treasury specifications for manganese borate require that it be free from by-products, and that, other properties being satisfactory, preference will be given to the article containing the least amount of alkali.

Another practical test much in vogue among practical painters and shop foremen is to make a semi-paste with moisture-free litharge and the drier. High-class driers will remain three to four days before showing a decided tendency to thicken or harden; cheap rosin driers will begin to harden in a comparatively short time.

CHAPTER XVIII.

ANALYSIS OF SHELLAC AND SPIRIT VARNISHES.

Analysis of Shellac.

350. The most common adulterant of shellac is common rosin or colophony. Sabin, in his Technology of Paint and Varnish, says that, " It is reported and probably true, that large quantities of common rosin are shipped to India and used as an adulterant of gum shellac."

351. **Detection of rosin.** About 1 gram of the sample is dissolved in about 15 c.c. of acetic anhydride, warming gently until the solution is complete. Cool thoroughly under the tap. The rosin will remain in solution while the greater part of the shellac will separate out. Filter. Place a few drops of the filtrate on a porcelain crucible, cover, and add by means of a stirring rod one drop of sulphuric acid (34.7 c.c. sulphuric acid and 35.7 c.c. water) so that it will mix slowly. If rosin is present a characteristic violet fugitive color results. A pure shellac should give no coloration.

352. **Estimation of rosin.** The amount of rosin present is best estimated by means of the iodine number. For this purpose the Hanus method is to be preferred to the Hubl or Wijs method. The Hubl for a long time has been the official method, but it has several faults which affect its accuracy. It rapidly loses strength and is so slow in its reaction with some oils, such as linseed oil, that a serious error is brought about by the change in strength of the solution during the reaction. Another objection to the

Hubl method is that practically each chemist uses a modification of his own as regards the time necessary for the solution to remain in contact with the substance to be tested.

In their workings the Hanus and Wijs methods are very similar, but the Hanus solution is much easier to prepare and the results obtained more nearly correspond to those obtained by the Hubl method. As most of the published data relating to the iodine numbers of oils, fats, etc., has been obtained by the use of the Hubl method, this fact is of considerable importance in making comparisons.

353. The Hanus solution is prepared and used as described in Chapter IV.

0.2 gram to 0.3 gram of the ground sample is introduced into a 250 c.c. Erlenmeyer flask; 20 c.c. of glacial acetic acid added, and the mixture warmed until the solution is complete, except for the wax. 10 c.c. of chloroform is added, the solution cooled to room temperature, and 25 c.c. of Hanus solution added, the flask stoppered, allowed to remain in the dark or in diffused light for 1 hour, with occasional shaking. 10 c.c. of potassium iodide solution is then added, 100 c.c. of water and titrated with tenth-normal thiosulphate, using starch as an indicator in the usual manner. Blank determinations should be made each time.

EXAMPLE:

Wt. of sample = 0.4 gram.

A blank of 25 c.c. of Hanus solution required 55 c.c. of thiosulphate.

One c.c. of thiosulphate = .0125 gram of Iodine. Titration of unabsorbed iodine = 49.5 c.c. thiosulphate.

55.0 − 49.5 = 5.5 c.c. of thiosulphate equivalent to iodine absorbed.

$(5.5 \times 100 \times .0125) \div 0.4 = 17.2$ per cent iodine absorbed.

354. Iodine Numbers of shellacs obtained from the leading wholesalers and jobbers of the United States, supposed to be strictly pure:[1]

No.	Variety.	Iodine No.	Color Reaction.[2]
1	Orange shellac	31.06	Rosin present.
2	Unbleached shellac	15.85	Rosin absent.
3	Orange shellac	12.68	Rosin absent.
4	Ralle standard shellac	16.80	Rosin absent.
5	Star brand shellac	14.90	Rosin absent.
6	H. N. superior shellac	12.99	Rosin absent.
13	Orange shellac	22.27	Rosin present.
14	Orange shellac	20.36	Rosin absent.
15	Orange shellac	16.54	Rosin absent.
16	Orange shellac	20.36	Rosin absent.
17	Orange shellac	13.36	Rosin absent.
7	Bone Dry bleached shellac	8.87	Rosin absent.
8	Refined bone dry bleached shellac	12.34	Rosin absent.
9	Bleached shellac	6.34	Rosin absent.
10	Bleached shellac	8.87	Rosin absent.
12	Bleached shellac	13.36	Rosin absent.

Analysis of Shellac Varnish.

355. Composition. A varnish having the proper consistency is prepared by dissolving 45 parts of shellac in 55 parts of grain alcohol of 94 per cent strength or about 5 pounds of shellac per gallon of alcohol. In place of the expensive grain alcohol, some manufacturers substitute wood alcohol or Columbian spirits, which is rectified wood alcohol. The poisonous properties of wood alcohol are well known, and on account of its injurious effects great care should be exercised in the use of varnishes containing it. Shellac varnish is often adulterated with rosin, thus producing a product of an inferior quality. The sophis-

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[1] Analyses by author.

[2] Libermann-Storch Reaction.

tication of varnish with this substance is well described by Langmuir:[1] "Starting out with an adulterated shellac, the varnish maker, secure in his belief that rosin cannot be detected in the solution, proceeds to add still more rosin. What has been said in regard to adulteration of shellac fades into insignificance in comparison with that practice in the manufacture of shellac varnishes. Shellac varnishes are sold containing no shellac. 'Pure' shellac varnishes, grain alcohol, may be purchased at less cost than the alcohol."

356. Determination of the body of shellac varnishes. Three to 5 grams of the well stirred sample is weighed into a weighed flat-bottomed petri-dish and evaporated to a constant weight in the steam oven. The result is calculated in pounds per gallon. If a platinum evaporating dish be used and the evaporation conducted over a water bath, the amount taken should not be over 1 gram. Taking the weight of a gallon of wood alcohol at 60°F. as 6.75 pounds, the pounds per gallon may be ascertained by means of the following table:[2]

Per cent. Residue.	Pounds per Gallon.
30.77	3.0
34.15	3.5
37.20	4.0
40.00	4.5
42.55	5.0
44.90	5.5
47.06	6.0
49.05	6.5
50.91	7.0
52.63	7.5
54.23	8.0

357. Determination of the strength of the alcohol used. The strength of the alcohol may be calculated, knowing the

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[1] Determination of Rosin in Shellac, J. Soc. Chem. Ind., January 1, 1905.

[2] Determination of Rosin in Shellac, J. Soc. Chem. Ind., January 1 1905.

per cent of residue as determined above and the specific gravity of the varnish. The calculation is best illustrated by the following example:

5 grams of varnish yielded a residue of 2.300 grams.

The specific gravity of the varnish was 0.9445 at 15.5° C.

100 grams of the varnish gave 2.300 × 20 = 46.00 grams of residue or 46.00 per cent.

The alcohol by difference 100.00 − 46.00 = 54.00 grams or 54.00 per cent.

Average specific gravity of shellac itself = 1.145.

The volume taken up by the shellac in the varnish would be 46.00 ÷ 1.145 = 40.17 c.c. in 100 grams of varnish.

The specific gravity of the varnish was 0.9445.

100 c.c. would weigh 94.45 grams and hence 100 grams would occupy 105.9 c.c.

105.9 c.c. − 40.17 c.c. = 65.73 c.c., the volume occupied by 54.00 grams of alcohol solvent.

54.00 ÷ 65.73 = 0.8215, the specific gravity of the alcohol. From the alcohol tables this will be found to correspond to 90.5 per cent of grain alcohol. If desired a portion of the varnish may be distilled until the decomposition point is reached and the strength of the alcohol determined from the specific gravity of the distillate.

358. Examination of the solvent. One hundred grams of the varnish is carefully distilled to the point of incipient decomposition. If necessary the distillate may be redistilled.

359. Detection of benzine. Dilute a portion of the distillate with three or four volumes of water. If benzine is present it will separate out.

360. Columbian spirit and wood alcohol. The test for acetone, which is always to be found in wood alcohol, will distinguish between Columbian spirit and wood alcohol.

361. Detection and estimation of wood alcohol in mixtures with grain alcohol. Qualitatively, the methyl alcohol may be detected by the following method:

Dilute a portion of the distillate until the liquid contains approximately 12 per cent of alcohol by weight.

Oxidize 10 c.c. of the liquid in a test tube as follows: Wind copper wire 1 m.m. thick upon a rod or pencil 7 to 8 m.m. thick in such a manner as to enclose the fixed end of the wire and to form a close coil 3 to 3.5 cm. long. Twist the two ends of the wire into a stem 20 cm. long and bend the stem at right angles about 6 cm. from the free end, or so that the coil may be plunged to the bottom of a test tube, preferably about 16 m.m. wide and 16 m.m. long. Heat the coil in the upper or oxidizing flame of a Bunsen burner to a red heat throughout. Plunge the heated coil to the bottom of the test tube containing the diluted alcohol. Withdraw the coil after a second's time and dip it in water. Repeat the operation from three to five times, or until the film of copper oxide ceases to be reduced. Cool the liquid in the test tube meanwhile by immersion in water.

362. Add 1 c.c. of strong ammonia to the oxidized liquid in a casserole and expel the acetaldehyde by boiling gently over a direct flame until the vapor ceases to smell of ammonia. Add 2 to 3 drops of strong hydrochloric acid to set free the formaldehyde which has been retained as hexamethyltetramin, and bring the liquid momentarily to a boil; cool promptly by immersion of the casserole in water and test for formaldehyde by the modified resorcin test, as follows:

Add to the liquid remaining 1 drop of a solution containing 1 part of resorcin in 200 parts of water, and pour the mixture cautiously into a test tube containing 3 c.c. of concentrated sulphuric acid, holding the tube in an inclined position in such a manner that the two liquids shall not mix. Allow it to stand 3 minutes, then sway the tube slowly from side to side in such a manner as to produce a gentle rotary motion of the two layers. Persist in this operation, if necessary, for a minute or more, using a piece of white paper for a background, and producing only a very gradual and partial mixing of the acid and water. Nearly half of the acid should remain as a distinct unmixed layer at the end. When methyl alcohol is present, the shaking causes the separation of more or less voluminous flocks of a very characteristic rose-red color. The appearance of colored zones or flocks of other hues, even when tinged with red, or of a rose-red solution without flocks, should never be considered proof of the presence of methyl alcohol. However, if the flocks are reddish brown, or if the upper layer has a pronounced red, it is often well to repeat the test.

By this method for the removal of acetaldehyde 10 per cent of methyl alcohol may be readily detected, and an experienced operator may detect with certainty a less amount.

363. Quantitatively the methyl alcohol may be estimated by the method of Thorp and Homes.

This method depends upon the fact that in the presence of potassium dichromate and sulphuric acid in a closed vessel at 100°, ethyl alcohol is converted into its theoretical equivalent of acetic acid, while with methyl alcohol, the product resulting from the oxidation is always carbon dioxide and water. It has, however, been found that for each gram of ethyl alcohol present in the solution 0.01 gram of carbon dioxide may be formed, and this correction should be made in all determinations.

The specific gravity is determined by means of a pycnometer. The total per cent of the alcohol is practically the same as the per cent of ethyl alcohol of the same specific gravity.

364. The methyl alcohol is determined by converting it into carbon dioxide by means of sulphuric acid and potassium dichromate in the Knorrs' apparatus described under the estimation of carbon dioxide in white lead.

Weigh into the flask 20 grams of potassium dichromate, connect the apparatus after having weighed the soda-lime tubes. Introduce through the stop-cock funnel an exact volume of the alcohols not to exceed 4 grams of the mixed alcohols, and an amount of water equal to 50 c.c. less the number of c.c. of alcoholic solution, 80 c.c. of sulphuric acid (made by diluting one volume of concentrated acid with four volumes of water) are added, well shaken and allowed to stand 18 hours. Dissolve 10 grams of potassium dichromate in 50 c.c. of water, add through the funnel, then add 50 c.c. of concentrated sulphuric acid and heat the contents of the flask to boiling for about ten minutes, the carbon dioxide being carried off by a current of air through the apparatus. The heat is now removed and the current of air continued for a few minutes longer. Disconnect and weigh the soda-lime tubes.

Calculate the methyl alcohol from the proportion

$$1.373 : 1 :: \text{wt. } CO_2 \text{ obtained} : x$$
$$x = \text{wt. methyl alcohol,}$$

the theoretical oxidation of 1 gram methyl alcohol producing 1.373 grams of carbon dioxide.

EXAMPLE.

Specific gravity of sample,	0.7992
Weight of sample used,	1.0118 grams
Weight of carbon dioxide,	1.3810 grams

$1.373 : 1 :: 1.3810 : x$

$x = 1.006$ grams methyl alcohol.

$1.0118 : 1.006 :: 100 : y$

$y = 99.4$ per cent methyl alcohol.

365. If ethyl alcohol is present, the correction previously referred to, of 0.01 gram carbon dioxide for each gram of ethyl alcohol, should always be applied. The weight of the methyl alcohol subtracted from the weight of the mixed alcohols (calculated from the sp. gr.) gives the weight of the ethyl alcohol, approximately. The weight obtained by 0.01 gives correction to be deducted from the total carbon dioxide, for the recalculation of the weight of methyl alcohol. It is obvious that a very slight error is thus introduced, but the writer believes that it is so small that it may be safely neglected.

366. **Detection and estimation of rosin.** The residue remaining after the drying of the varnish in the determination of the " body " may be used for the detection of rosin as described under the examination of shellac.

If much rosin is present, it is not safe to take the residue after evaporation for the quantitative estimation as has been shown by Langmuir. " A little rosin (iodine value 224.3) was dissolved in alcohol, evaporated on the water bath and heated 5 hours. It then showed a value of 148.2. Similarly, a dark rosin 175.7 fell to 131."

A quantity of the varnish sufficient to yield 0.2 to 0.4 gram of residue is weighed from a small vial, provided with a perforated stopper carrying a shortened 1 c.c. pipette, into a 200 c.c. Erlenmeyer flask; the weight of the sample used being thus obtained by difference. The sample in the flask is carefully evaporated at a low temperature until pasty and then dissolved in the requisite amount of acetic acid and chloroform and the iodine number then determined in the usual manner. The error due to the action of the small amount of alcohol remaining in the pasty mass on the thiosulphate is negligible.

In calculating the per cent of rosin the iodine values of 150[1] for rosin, 16[1] for unbleached and 11[1] for bleached shellac may be used. If other resins are present, as sandarac, etc., these can only be calculated in the terms of rosin.

367. Estimation of rosin, Mannhardt's method.[2] Five grams of gum shellac or 10 grams of shellac varnish are weighed into a casserole or flask, and the solvent expelled on the water-bath. The residue is saponified with alcoholic potash, the alcohol expelled, and the residue taken up in 100 c.c. of hot water. At this point any wax present may be extracted with benzine (sp. gr. .730), the benzine evaporated off, and the residue weighed.

The solution of the soaps is treated with 50 c.c. benzine (sp. gr. .730), shaken vigorously, and, before the emulsion has time to separate out, add dilute sulphuric acid in slight excess. The shellac acids immediately coagulate, and all rosin acids go into the benzine, which is readily separated, filtered and evaporated in a weighed beaker. The shellac acids are absolutely insoluble in benzine. Damar and possibly sandarac will behave like rosin.

368. Practical test for brewers' varnish. Varnishes for brewers' purposes should be made from pure shellac and grain alcohol 94 per cent strength. They may be tested out by varnishing a strip of wood 6 inches long by 3 inches wide, and a quarter of an inch in thickness, and after drying immerse half of the strip in 4 per cent alcohol for 48 hours. A varnish made from impure shellac or alcohol of less than the proper strength will soon turn white.

[1] Average values obtained by author.

[2] Hans Mannhardt, Chemist, Heath & Milligan Mfg. Co.

369. ANALYSES OF SHELLAC VARNISHES.[1]

No.	Variety.	Iodine Number.	Percentage of Gum.	Calculated Percentage Rosin.
18	Orange shellac . . .	40.5	49.8	18.3
19	Orange shellac	13.4	42.2	. . .
23	Orange shellac	26.2	37.1	7.6[2]
25	Orange shellac	16.2	35.9	. . .
26	Orange shellac	15.2	21.0	. . .
27	Orange shellac	37.4	13.3	16.0
29	Orange shellac	23.3	40.5	5.4[2]
31	Orange shellac	15.0	39.8	. . .
20	White shellac	40.8	44.1	21.4
30	White shellac	37.8	22.4	19.3
21	White shellac	13.3	41.0	. . .
22	White shellac	16.2	37.6	. . .
28	White shellac	17.5	42.0	. . .

370. Damar varnish. The following specifications adopted by the Navy Department, May, 1904, will serve for the practical testing and valuation of damar varnish.

Damar varnish must be made from the very best quality of damar gum in a solution containing at least 50 per cent of gum and 45 per cent of turpentine, the gum to be digested cold and well settled. The varnish must be as clear as and not darker than the standard sample, and must be free from benzine, rosin, lime, or other mineral matter. Its specific gravity at 60° F. must be about 0.950, and its flash point between 105° and 115° F. It must set to touch in not more than 20 minutes, and when mixed with pure zinc oxide must show a smooth glossy surface equal to that shown by the standard sample.

371. Tests. Besides chemical tests to determine the above qualities, and practical tests to determine its qualities of finish, a board properly coated with a mixture of

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[1] Analyses by author.

[2] Liebermann-Storch reaction produces a somewhat different color than that usually given by rosin, hence these samples may be adulterated with other gums.

zinc and the liquid will be exposed to the weather for a period of 1 month, and at the end of this time must have stood exposure equally as well as the standard sample. A similarly prepared sample will also be baked at 250° F., and must not at this temperature show any greater signs of cracking, blistering, or any other defects than standard samples under the same conditions. Another sample, similarly prepared, will be exposed in a dark room at ordinary temperature for a period of 1 month and at the end of this time must not have turned darker to any appreciable degree than the standard sample.

CHAPTER XIX.

ANALYSIS OF OIL VARNISHES.

372. Analysis of oil varnishes. As stated by Hurst, "The analysis of oil varnishes is one of great difficulty, as it is quite impossible to separate all the ingredients from one another." However in spite of the unsatisfactory state of our present knowledge of varnish analysis, a distillation and separation will give an approximate idea of the quantity and kind of volatile solvents used. Treating the residue by Twitchell's method, will give approximately the amount of oil and the amount of gum present in the varnish and an examination of the physical and chemical properties of the separated gum may give an approximate idea of its hardness, and throw some little light on its probable source. The presence of lime, color produced by the Liebermann-Storch reaction, acid figure and iodine absorption will indicate the presence of rosin and to some extent the amount present. With these tests, in conjunction with the solubility of the separated gum, the original character of the varnish, e.g., the pouring of a portion of the sample on a sheet of glass, noting how it flows, dries, the kind of film produced, its resistance to abrasion, to moisture, its elasticity, etc., and a comparison made with varnishes of known composition and similar properties, a very shrewd guess can be made as to how the varnish under consideration must be duplicated, or in other words, the approximate amounts of the different gums required to produce a similar product.

373. On the other hand, a proximate analysis of a varnish furnishes us with but a small amount of helpful information, as the gloss, working qualities, and durability depend largely on the quality of gum used, the quality and treatment of the oil, the quality of the driers used, and especially as to how the varnish was prepared, as regards heat, method of cooking, ageing, filtering, etc. On these essential points a chemical analysis tells us but little. That greater light will eventually be thrown on the problems involved, the author has not the slightest doubt, but meanwhile interpretations based solely on chemical analyses are liable to be more or less misleading; but taken in connection with physical tests, carefully made, the value of varnishes can be determined with considerable accuracy.

374. **Specific gravity.** The determination of the specific gravity is of considerable importance and should be made with a pycnometer at 15.5° C.

375. **Viscosity.** The determination of the viscosity of a varnish will throw considerable light on its working qualities. Any of the standard types of viscosimeters may be used for varnish work, but the Doolittle Torsion Viscosimeter offers several advantages over the others.

376. **Separation, identification, and estimation of the volatile oils.** Seventy-five grams of a uniform sample of the varnish is weighed into a 500 c.c. distilling flask, provided with a tube leading very nearly to the bottom, the other end of which is connected with a steam supply. The flask is also provided with a thermometer, the bulb of which dips below the surface of the varnish, and the flask then connected with a rather long condenser. By means of an oil bath the varnish is heated to 130° C., and a current of steam passed through, until about 500 c.c. of water has passed over, or until the steam ceases to carry over any more volatile oil. It is advisable to collect the dis-

tillate directly in a separating funnel. When the volatile oil has completely settled out, the water is drawn off and the oil transferred to a weighed flask, weighed, and the percentage calculated. The aqueous distillate will contain a small quantity of the volatile oil equal to about 0.4 gram per hundred c.c. This correction should be made in calculating the percentage.

The constituents of the volatile oil and the amount of petroleum products present may be determined exactly as described in the chapter on the Analysis of the Vehicle of Mixed Paints.

377. **Separation of the resin gums from the oil, Twitchell's method.** The flask containing the residue of oil and gum is connected with a return condenser, 150 c.c. of normal alcoholic potash added, the flask heated carefully on a water bath to avoid bumping and finally heated over a free flame for about an hour. The solution is then cooled and separated from the residue, which is again treated with alcoholic potash, and the process continued until as complete a saponification as possible has been made; usually a small residue of about 1 per cent remains. The different alcoholic solutions are united, neutralized with hydrochloric acid, the excess of alcohol evaporated off, and the fatty acids and gums removed with successive portions of ether. The ethereal solution is distilled to remove the ether, a small quantity of absolute alcohol added, and the flask again heated gently, the alcohol carrying off the last traces of water. About 10 volumes of absolute alcohol are added to the dry gums and acids, the solution being kept cold by ice and dry hydrochloric acid gas is passed in until the solution is saturated. This will usually take from 30 to 45 minutes. The flask and contents are allowed to stand for about an hour, then diluted with about 5 volumes of hot water, and boiled

until clear; the heating being conducted gently to avoid frothing.

378. The contents of the flask are mixed with a little petroleum ether, boiling below 80° C. and transferred to a separating funnel, the flask being washed out with the same solvent. The petroleum ether layer should measure about 50 c.c. After shaking, the acid solution is run off and the petroleum ether layer washed once with water, and then treated in the funnel with a solution of 2.5 grams of potassium hydroxide and 20 c.c. of alcohol in 200 c.c. of water. The ethylic esters dissolved in the petroleum ether will then be found to float on top, the rosin acids having been extracted by the dilute alkaline solution to form rosin soap. The soap solution is then run off, decomposed with hydrochloric acid, and the separated rosin acids collected as such, or preferably dissolved in ether, and the whole evaporated in a small weighed beaker on the water bath. A small quantity of absolute alcohol is added, and the evaporation repeated. Finally, cool in the desiccator and weigh. This will give approximately the amount of gums present in the varnish. Any residue insoluble in the 10 volumes of absolute alcohol above mentioned is weighed up and its weight added to the weight of resin gum.

379. **Separation of the gums from the oil, Scott's Method.**[1] In separating the gum, by this method, it is necessary to know whether the sample is a Long Oil or Short Oil Varnish, i.e., whether it contains a large or small amount of linseed oil. Hard oil finishes, interior varnishes, and rubbing varnishes are usually shot oil varnishes, while carriage and similar varnishes are long oil varnishes.

In order to determine to which class a varnish belongs,

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[1] Drugs, oils, and paints, XV., No. 4, p. 132, and No. 6, page 219.

about 10 c.c. of the sample is poured into a beaker and 50 c.c. of benzine, previously cooled to about 5° C., added. If the sample be short oil varnish the gums will be partially precipitated, while a long oil varnish will show but little change. The color of the precipitated gum may be considered as another indication, a light colored precipitate denoting a short oil, and a dark colored preciptate, a long oil varnish.

380. **Short oil varnishes.** A beaker of about 150 c.c. capacity, provided with a stirring rod, is carefully weighed, and about 10 grams of varnish weighed into it. Cool to below 10° C. Fifty c.c. of petroleum ether that has previously been cooled to below 3° C. is poured into the beaker and the contents stirred. The beaker is placed in a freezing mixture for about an hour, or until the precipitated gums have settled.

381. Place a filter paper that has been dried in the oven, in the suction funnel. Moisten and suck the filter free from surplus moisture, pour in the gasoline, retaining as much of the resins as possible in the beaker. Add another 50 c.c. of ice cold petroleum ether, and allow to stand as before in the freezing mixture. Meanwhile pour 25 c.c. of ice cold water on the filter paper, allowing it to run into the petroleum ether filtrate, which is then vigorously shaken up so as to thoroughly mix the water and petroleum ether, which causes the gum held in solution by the ether to precipitate, and on refiltering is retained. The second ether solution that has been cooling is now poured on to the filter along with the precipitate, rinsing out the beaker with ice cold petroleum ether. Treat with 25 c.c. of ice cold water, shaking and refiltering, as described above. Repeat this operation twice, transfer the filter, and precipitate to the weighed beaker, and dry in the hot air oven at 105° to 115° C. and weigh.

Increase in weight, over that of the beaker, stirring rod and filter, represents the weight of the gum.

The petroleum ether solution containing the varnish oils is poured into a weighed beaker, the excess of petroleum ether evaporated off with due precautions, and the beaker placed in the hot air oven for 3 hours at 150° C., cooled and weighed. The residue represents the fixed oils in the varnish.

382. Long oil varnishes. Distil off the thinners from a portion of the sample. Weigh out 10 grams of the gum and oil into a weighed beaker as described above, cool down below 15° C. and add 50 c.c. of petroleum ether cooled below 0° C. Set in the freezing mixture for an hour and finish exactly as described under short oil varnishes. The separation of the total gum in long oil varnishes is quite difficult and requires considerable patience and experience. According to the experience of the author, Scott's method gives somewhat low results, especially as rosin is quite soluble in cold petroleum ether.

383. Determination of the so-called insoluble and soluble gums. This method is somewhat similar to the above, and, in the hands of a careful chemist, when run alongside of standard varnishes, will throw considerable light on the nature of the sample in question.

Weigh 2 grams of the sample into a weighed 6-oz. wide-mouth flask, add 2 c.c. of chloroform, 100 c.c. of 80° petroleum ether, gradually and with constant shaking so as to avoid any preciptation, until 15 c.c. are added, allow to stand over night. The precipitated gums adhere to the bottom of the flask. Decant and wash with a little petroleum ether. Dry to constant weight as insoluble gum.

The petroleum ether extract should be decanted into a weighed beaker, the petroleum ether evaporated off and the beaker dried at 100° for seven to eight days to constant weight. All linseed oil should now be in the form of linoxyn. Digest over night with chloroform, which will dissolve the gum, and leave the linoxyn undissolved. Filter through cotton wool. Evaporate off the chloroform, dry to constant weight in the steam oven and weigh as soluble gum.

A varnish to meet with the requirements of the United States Treasury Department, among other things, should contain not less than 25 per cent of best quality imported gums, and must not contain rosin or petroleum products.

Varnishes containing wood oil are liable to give misleading results by the above method, as the whole or a considerable portion of the wood oil will be precipitated by the petroleum ether, depending on the length of time and temperature to which the oil has been heated.

384. **Detection and estimation of rosin in varnishes.** Qualitatively rosin may be detected as follows: Pour about 5 c.c. of the varnish into a small separatory funnel, add about 5 c.c. of carbon bisulphide, shake and add 10 c.c. of acetic anhydride. Allow to stand until complete separation takes place. Draw off the lower layer, which is the acetic anhydride. Pour 1 or 2 c.c. of the acetic anhydride portion into an inverted crucible cover, add carefully, by means of a stirring rod, one drop of sulphuric acid (34.7 c.c. of sulphuric acid to 35.7 c.c. of water) to the edge of the cover, so that it will mix slowly with the acetic anhydride, if rosin is present a characteristic fugitive violet color will result.

385. The quantitative estimation of rosin in the presence of other varnish gums is a problem of especial difficulty. Gill,[1] suggests a method based on comparative ester values. The ester value being obtained by sub-

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[1] J. Amer. Chem. Soc. XXVIII., No. 12, page 1723.

tracting the free acid value from the saponification value. The gums are separated from the oils by Twitchell's method, the last traces of moisture being removed by drying over sulphuric acid. Gill obtains the following values for rosin and kauri.

Gum.	Saponification.	Free Acids.	Ester.	Average.
Pure rosin, No. 1 . .	182.3	160.1	22.2	
Pure rosin, No. 6 . .	185.7	161.7	24.0	23.1
Kauri, No. 1 . . .	124.2	41.0	83.2	
Kauri, No. 2	129.7	45.0	84.7	84.0

By the use of the usual formula

$$x = \frac{100\ (I - n)}{m - n}$$

the percentage of adulteration may be approximated, as described in the chapter on the Analysis of the Vehicle, in discussing cotton-seed oil.

387. Gill's method is open to considerable criticism, as he directs that the Free Acid Value be obtained by direct titration, and the Saponification Value by saponifying in practically an open flask. Dietrich[1] has shown that direct titration gives acid values far too low for all resin, because the complete neutralization of the rosin acid proceeds slowly. As an illustration of this point, Worstall[2] gives the following experiment:

"Several portions of a sample of Kauri, whose acid number has been accurately determined as 103, were weighed out and the acid number determined by indirect

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[1] Analyse der Harze, Balsane, und Gumminharze.

[2] Chemical Constants of Fossil Resins, J. A. Chem. Soc. XXV., page 860.

titration at different intervals of time. The results were as follows:

Time.	Acid No.
5 minutes	82
1 hour	92
3 hours	96
6 hours	101
12 hours	102
18 hours	103

388. Regarding open saponification Worstall states that " from the researches of Tschirch and his pupils, it appears that the copals consist of 'resenes' — neutral compounds containing oxygen and possibly of an aldehyde nature — and of the resin acids. Other investigators have noted the fact that the copals will absorb oxygen, and evidently the increase in acid number and decrease in iodine absorption is due to the oxidation of these 'resenes,' by contact with the air, to resin acids. . . . That this increase in the acid number is actually due to oxidation, the following experiments will illustrate:

"A number of samples of Kauri were selected, each one finely powdered, and its acid and iodine numbers determined. These samples were then left four months in open bottles exposed to the air, and the powdered resins stirred from time to time to promote oxidation. At the end of this time their constants were again determined with the following results.

No.	Before Acid.	Oxidation Iodine.	After Acid.	Oxidation Iodine.	Acid Increase.	Iodine Decrease.
1	72	154	87	133	15	21
2	76	159	111	121	35	38
3	77	140	93	115	16	25
4	72	170	107	110	35	60
5	97	109	104	99	7	0
6	105	113	109	112	4	1

"Samples 1, 2, 3 and 4 were hard, 'bold' gum of highest quality, while samples 5 and 6 were of a soft, spongy, lowest grade Kauri, in which oxidation had already made much progress before the experiment was carried out.

"This oxidation proceeds rapidly in presence of alkalies, so that open saponification with alcoholic caustic potash gives acid numbers that are much too high. Doubtless this fact, in connection with the impossibility of obtaining correct acid numbers by direct titration, has led to the reporting of ester values in resins where no esters exist. That Kauri is free from esters was shown by saponifying several samples in flasks with return condensers, digesting for one hour on the steam bath. In every case the saponification number thus found was the same as the indirect acid number."

389. From the above data it is evident that in order to approximate the percentage of rosin in a varnish by the so-called ester values according to Gill's method, each analyst must establish his own set of figures, under certain definite working conditions, obtaining his data from varnishes of known composition. Any variation of these conditions, either in time, factor or condition of the gums, is certain to give different results.

Little that is reliable has been written concerning the detection of the other varnish gums. Certain resins, however, give some indication of their presence. For instance, Kauri imparts a reddish stain to a varnish. Damar, if present in considerable quantity, can be detected by its smell, especially in the dried varnish. It is seldom found in varnishes intended for outside use.

390. In closing, a word should be said concerning wood oil. This product, the properties of which are but little understood by the majority of chemists, is finding a wide use among varnish manufacturers. It is claimed by var-

nish manufacturers that by the use of wood oil, varnishes containing a large amount of rosin may be prepared, possessing satisfactory wearing qualities and free from the objectionable features of ordinary rosin varnishes. However, in light of the rather heavy losses encountered by a number of varnish firms in endeavoring to prepare a satisfactory rosin-wood oil varnish, the above claims of the varnish manufacturers may be questioned somewhat. As to the analysis of this type of varnish the author is not aware of any suitable published method. It is said, however, that it may be detected qualitatively by practical varnishers, in quantities as low as five per cent by the characteristic odor given off in sandpapering a coat which has barely dried.

391. Navy specifications for interior varnish for naval vessels, 1906. To be of the best quality and manufacture and equal in all respects — including body, covering properties, gloss, finish and durability — to the standard samples in the general storekeeper's office, navy-yard, New York. To be made exclusively from the best grade of hard varnish resins, pure linseed oil, pure spirits of turpentine and lead manganese driers, and to be free from all adulterants or other foreign materials. The varnish must flash above 105° F., set to touch in from 6 to 8 hours, and dry hard within 24 hours in a temperature of 70° F. It must stand rubbing with pumice stone and water within 36 hours without sweating, and must polish in 72 hours with rotten stone and water. To be as clear and not darker than the standard sample, and to be equal to it in all respects as above specified.

392. Navy specifications for black asphaltum varnish, 1906. Black asphaltum varnish must be of pure, high-grade asphaltum of the very best quality, pure linseed oil, pure spirits of turpentine and lead manganese driers, and to be free from all adulterants or other foreign materials, and must contain not less than 20 gallons of prepared linseed oil to 100 gallons of varnish. It must not flash below 105° F. (open tester). It must mix freely with raw linseed oil in all proportions; must be clear and free from sediment, resin, and naphtha, when flowed on glass, and allowed to drain in a vertical position; the film must be perfectly smooth and of full body. It must set to touch in from 1½ to 2 hours, and dry hard in less than 20 hours at 70° F. When dry and hard it must not rub up or powder under friction by the finger. The application of heat must quicken the time of drying and give a harder film.

CHAPTER XX.

THE PRACTICAL TESTING OF VARNISHES.

393. The thorough practical testing of varnishes is an exceedingly difficult matter for the average chemist, as it requires long familiarity with the direct application of varnishes under a large variety of circumstances and conditions. However, there are several practical tests which can be made without special difficulty, and which will throw considerable light on the character of the varnish, especially if the chemist be supplied with a standard set of varnishes which he can run along with the sample to be tested, and have constantly by him to enable him to check up his judgment by comparison.

394. **Smell.** The smell of a varnish will often tell much concerning its value. A good, wholesome, gummy odor usually indicates a varnish made from good materials, while a strong, raw, pungent odor is often the sign of a cheaper grade of goods. Markedly inferior articles can almost without exception be detected in this manner. Occasionally the true odor of the varnish is masked by a strong turpentine odor, in which case allow a sample of the varnish to drain out of a beaker for 3 to 5 minutes and then note the smell of the portion adhering to the sides of the beaker, i.e., the "after smell," as it is called.

395. **Consistency.** The consistency of a varnish is to a considerable degree regulated according to the work for which it is to be used, and should be judged accordingly. There is a marked tendency, at the present time, to make varnishes altogether too thin. This may in part

be due to the insistent demands made by contractors and other varnish users for goods that will " work fast " and dry quickly, but it should be remembered that such varnishes do not afford the measure of protection to the surface that is regarded necessary by the best practical users of varnish.

396. **Working and flowing.** The working qualities of the varnish under the brush will at once show whether the chemist is dealing with a " long oil " or a " short oil " varnish. A test board having been suitably surfaced and filled either with thin shellac, or with the varnish reduced with 25 per cent of turpentine, dried and sandpapered down smooth, is given an even, uniform coat of the varnish to be tested. The length of time the varnish can be worked under the brush, before it exerts a characteristic " pull " on the brush, is indicative of the character of the varnish. If it permits of sufficient time for thorough brushing out so that a large panel could be coated and worked out smooth, before it begins to pull on the brush, i.e., " set up," the sample would be considered a long oil varnish, while if it begins to pull under the brush almost at once, it would be considered a short oil varnish. Naturally, there are varnishes which do not exhibit these extremes, but usually the classification can be made without difficulty.

397. Special notice should be taken of the way the varnish flows out into a uniform surface, whether it does so with ease, or slowly and with difficulty. In applying the final coats the working and flowing can be studied with greater exactness. Some varnishes will work easily, others will work " tough," some " greasy," etc.; with a little experience the chemist can grade them with considerable accuracy. As mentioned in a preceding paragraph, there are many varnishes on the market which are altogether too thin. Such varnishes will work and flow

with great ease because of their excessive thinness, and hence the consistency must be taken into account when passing on the working and flowing qualities.

398. Time of drying. The time a varnish requires to dry properly, i.e., to harden thoroughly, is regulated according to the purpose for which the varnish is to be used. For instance, floor varnishes are supposed to dry hard over night, while the average spar varnish will require a much longer time. Hence the samples tested should be compared with the accepted standards of those types of varnishes, both on the wood test surface and on a sheet of glass, on which samples of the varnishes have been placed and then set in a dust-free but unconfined place at an angle of about 30 degrees from the perpendicular. The best results are secured by resting the glass on a couple of small hooks, which permits the varnish to drain freely. The rapidity of the drying should be noted at regular intervals. When dry, the tests should be saved for further examination.

399. The sponge test. After the requisite number of coats have been applied to the test boards and the finishing coat has hardened thoroughly, a sponge made of several thicknesses of felt is thoroughly moistened and laid on the varnished surface and allowed to remain for a stated number of hours, undisturbed. A high-grade varnish will either show no discoloration at all, or will regain its color on drying, provided, of course, that it has been suitably applied. A varnish containing a large amount of rosin will be more or less badly corroded and will remain permanently white and discolored. With a little practice by working with varnishes of known composition the chemist can make a pretty shrewd guess as to the approximate amount of rosin present by the degree of discoloration. Right here the author wishes to state that the use of cheap inferior rosin varnishes has caused untold damage. There is probably more rosin varnish sold than all other grades put together. It is claimed by high-class manufacturers that the addition of three or four per cent of hardened rosin will enable the varnish maker to melt his gums at a somewhat lower heat and without darkening, thus making a better and lighter-colored varnish; but the addition of rosin has passed this point so far that a three or four per cent addition is a very minor consideration indeed.

400. Another modification of the above test is to varnish a clean strip of tin, and after thorough drying immerse it under water and note the rapidity and extent of corrosion and discoloration.

401. **Toughness and elasticity.** In order for a varnish to be durable and give entire satisfaction, it must have the desired toughness and elasticity as well as the requisite hardness. A varnish which is brittle, although it may have the required hardness, will be easily cracked or crushed by a very moderate blow. Some varnishes are required to be tougher and more elastic than others, as in the case of floor finishes.

402. The varnish having thoroughly dried on the test glass alongside of the standard sample, its toughness may be determined to a certain extent by its behavior under the thumb-nail, and the results obtained compared with a similar examination on the varnished test board. Also the films of the thoroughly dried varnish on the test glass may then be scratched with a sharp instrument. A small, sharply pointed knife-blade is excellent for this purpose. A first-class varnish having suitable toughness and elasticity will show a smooth, even scratch, no scaling or " dusting " being observable; and if the knife be held in the proper position, a small uniform, coherent ribbon of varnish will be ploughed off. If the varnish is deficient in elasticity and toughness, it will scale away under the knife-point,

exhibiting a ragged, irregular scratch. Varnish films containing rosin when tested with the knife-point will usually "dust" more or less badly, i.e., fly away from the knife-point in the form of a fine powder, settling on the glass at a considerable distance from the scratch. The fact that varnishes vary greatly in consistency should be taken into account in making these tests, as the films on the glass will vary in thickness according to the consistency of the varnish.

403. In judging the brittleness of a varnish on a test board, especially if it is hard wood, the effect of the material used for the first coat must be taken into consideration. This may be readily shown by taking a hard-wood board, coating a portion of it with shellac, another portion with an average cheap liquid filler, and the remaining portion with the varnish itself. After applying two coats of varnish over the entire surface and allowing it to harden thoroughly, it will be found on testing the surface with a knife that the varnish over the liquid filler is very brittle, that over the shellac somewhat brittle, while the straight varnish-filled surface will remain tough and elastic. Another method of testing the elasticity, is to varnish a strip of tin, and, after thorough drying, bend the tin and note the extent which the varnish gives under the strain to which it is subjected. In making these various tests, the chemist must be certain that the varnish is thoroughly dry, as many of the cheaper varnishes harden slowly, and, if examined too soon, will show greater toughness and elasticity than would be obtained in actual practice.

404. **Hardness.** A varnish may have the toughness and elasticity required of first-class goods, but may be deficient in hardness. In order to report on the hardness, the chemist should have some means of giving this quality a numerical value. An instrument for this purpose has been

devised by Dr. A. P. Laurie and F. G. Baily of Heriot Watt College, Edinburgh, the essential features of which are a central rod sliding easily in a vertical direction through holes in two brackets. The upper portion of the rod has a screw thread, on which is a running nut. By means of a milled head at the top the rod is twisted round, and the nut caused to travel up and down on the thread. A spring is attached at its upper end to the travelling nut and at the lower end to the lower bracket. To the lower end of the rod is attached a hardened blunt steel point, and the varnished plate to be tested is placed under this point, and the point brought to the surface of the varnish. The test surface is drawn slowly under the point, the pressure being increased until a white scratch is observed, at which point the reading is noted on the scale. The machine reads to a maximum of 2000 grams. Spirit varnishes break down at a pressure of about 100 grams, rosin varnishes 200 to 400 grams, fairly good common varnishes at about 700 grams, and fine carriage varnishes at 1200 grams and upwards. The inventors claim that the best oil varnishes take twelve months to reach their maximum hardness, and that the rate of drying and the ultimate hardness can be measured with accuracy by their instrument.

405. **Classification of varnishes.** The varnish industry has from its beginning been conducted with as much secrecy as possible, and but little has been published that would enable the average chemist to pass judgment on the different grades and varieties of varnish, and for this reason a short discussion of some of the principal classes of varnish may not be amiss.

406. **Floor varnishes.** Goods of this class should have a medium consistency. If heavy they will require a longer time to dry and harden than is desirable, and would be apt to become marred from usage before thoroughly hardened;

if too thin they will not afford the desired protection to the wood. In price they are about the same as for first-class interior varnishes, ranging usually from $2.00 to $2.50 per gallon wholesale. Floor varnishes are usually " long oil " goods, as a high degree of elasticity is required.

407. **Interior varnishes.** Varnishes for interior work should be of fairly heavy consistency, so as to stand rubbing. For the best class of work they should be " long oil," although " short oil " goods may be used for the undercoats. In price they usually range from $2.00 to $2.50 per gallon wholesale. Often, especially in contract work, " No. 1 Coach " goods are used. This term means absolutely nothing, as it stands for no specific grade or quality of varnish. Sold under this name varnishes are put on the market for $0.90 to $1.10 per gallon, or even less, and are usually high in rosin and benzine or heavier petroleum-products. Polishing varnishes, such as are used for pianos, high-class furniture, etc., are usually of excellent quality, averaging in price from $2.50 to $2.75, although the very best grades may run as high as $3.50 wholesale.

408. Interior varnishes being subjected to less strenuous usage than floor finishes, carriage or exterior goods, the tendency has been to lower the standard of quality, until perhaps low grade, inferior goods are the rule, and really high-grade finishes the exception, on the market at the present time. Neither is the size of the company any guarantee that the product is of high value, for many of the best grades of varnishes are made by small concerns who depend on the quality of their goods rather than on extensive advertising for their sales.

409. **Exterior varnishes.** These should always be " long oil " goods. Spar varnishes, which are the usual type of exterior varnishes, should be of medium consistency, tough and elastic, and not easily scratched. In price they

usually range from $3.00 to $3.75 per gallon wholesale. Carriage varnishes bring the highest price of all varnishes, and their successful manufacture is accomplished by only a comparatively small number of concerns, and but few domestic brands are rated equal to the best imported English goods. Domestic carriage varnishes range from $4.75 to $5.75 wholesale, and the best imported English goods at about $7.25 per gallon.

410. Short volume. It is a lamentable fact that varnish manufacturers almost invariably defraud the consumer by putting out their packages short in volume. Of eleven samples purchased by the author on the open market, in the original package none were full measure. The amount of shortage is given in the following table:

No.	Description.	Per Cent Shortage of Contents.
1	Floor Varnish.	3 .2
2	Floor Varnish.	4 .2
3	Floor Varnish	2 .1
4	Interior Varnish	3 .2
5	Exterior Varnish	2 .1
6	Coach Varnish	2 .1
7	Interior Varnish	8 .4
8	Floor Varnish	3 .2
9	Exterior Varnish	4 .2
16	Floor Varnish	9 .5
18	Floor Varnish	13 .3
	Average	5 .0

Five per cent shortage in measure represents a very fair profit to the manufacturer in itself.

411. Significance of lime in varnishes. The addition of five to six per cent of quicklime to melted rosin makes it considerably harder. The compound formed easily dissolves in linseed oil (at the present time wood oil is largely used), and when properly thinned forms the base of about all the cheap varnishes on the market. Such varnishes are characterized by giving a brilliant surface, easily scratched, and in a short time liable to crack badly. The relation between the percentage of lime (CaO) in the varnish and its toughness and elasticity is not marked enough to enable the chemist to pass judgment on its working qualities from the amount of lime it contains.

412. Sixteen of the leading varnishes on the market were tested out for toughness and elasticity, and then the amount of calcium oxide determined in each, the results obtained being given in the following table.

No.	Kind.	Per Cent of Calcium Oxide in Varnish.	Elasticity and Toughness.
2	Floor Varnish	0.868	Good
3	Floor Varnish	0.246	Good
4	Interior Varnish	0.200	Good
5	Exterior and Interior Varnish	0.178	Medium
6	No. 1 Coach Varnish . . .	0.313	Good
7	Interior	0.195	Poor
9	Exterior	. . .	Medium
11	No. 1 Coach Varnish . . .	0.265	Poor
13	Interior Varnish	0.271	Very Poor
14	Interior Varnish	0.161	Poor
15	Coach Varnish	0.800	Medium
17	Interior Varnish	0.158	Medium
19	Interior Varnish	0.158	Good
21	Interior Varnish	0.212	Good
23	Interior Coach Varnish . .	0.532	Poor
25	Interior Varnish	0.281	Poor

413. Of twelve brands of floor varnishes examined by the author, four were altogether too thin for the purpose intended; and of fourteen interior finishes, four were exceedingly thin, and several of the remainder were below average in this respect.

Of a total of twenty-six of the leading brands of floor, exterior and interior varnishes tested out by the author, seven were considered first class in all respects, eight were medium or just fair quality, while eleven were unquestionably poor and inferior both as regards working and the quality of the film after drying. Of the above eleven, eight were interior finishes.

414. The twenty-six with but two exceptions flashed at room temperature, a fact which is worthy of considerable attention on the part of the consuming public as regards fire risk.

APPENDIX.

415. TRADE NAMES OF THE PRINCIPAL PAINT PIGMENTS WITH CHEMICAL NAMES.

BLUE PIGMENTS.

Trade Name.	Composition.
Antwerp blue	Potassium ferric ferrocyanide.
Chinese blue	" " "
Cobalt blue	A compound of the oxides of alumina and cobalt.
Prussian blue	Potassium ferric ferrocyanide.
Ultramarine	Exact constitution unknown.

RED AND YELLOW PIGMENTS.

Trade Name.	Composition.
American vermilion	Usually basic chromate of lead, sometimes an eosine vermilionette on red lead.
Chinese vermilion	Sulphide of mercury.
Chrome yellow	Lead chromate usually containing lead sulphate.
English vermilion	Sulphide of mercury.
Indian red	Natural oxide of iron about 90 per cent or more, pure.
Litharge	Lead monoxide.
Lemon chrome	Usually a mixture of lead chromate and lead sulphate.
Ochre	Earthy base carrying about 20 per cent hydrated ferric oxide.
Orange chrome	Lead chromate.
Para vermilion	An organic red precipitated on an inert base.
Permanent vermilion	
Radium vermilion	Red lead coated with organic color.
Tuscan red	A more or less impure oxide of iron brightened with organic color.
Venetian red	Usually a mixture of oxide of iron and calcium sulphate.

WHITE PIGMENTS.

Trade Name.	Composition.
Barytes	Barium sulphate.
Blanc fixé	Precipitated barium sulphate.
China clay	Hydrated silicate of aluminum.
Corroded lead	Basic lead carbonate.
English white	Calcium carbonate.
Gypsum	Hydrated calcium sulphate.
Lithopone	A combination of barium sulphate, zinc oxide and zinc sulphide.
Magnesite	Magnesium carbonate.
Marble dust	Calcium carbonate.
Paris white	Calcium carbonate.
Ponolith	Similar to lithopone.
Silex	Silica.
Silicate of magnesia	Magnesium silicate, aluminum, and calcium are usually present.
Silver white	Silica.
Spanish white	Calcium carbonate.
Standard zinc lead white	Lead sulphate and zinc oxide in about equal amounts.
Sublimed white lead	Apparently a basic sulphate of lead with about 5 per cent zinc oxide.
Terra alba	Hydrated calcium sulphate.
White lead	Basic carbonate of lead.
Whiting	Calcium carbonate.
White mineral primer	Calcium carbonate.
White ochre	Calcium carbonate.
Wood filler	Silica.
Zinc white	Zinc oxide.
Zinc oxide (leaded)	Zinc oxide containing a varying amount of lead sulphate.

BLACK PIGMENTS.

Trade Name.	Composition.
American gas black	Very nearly pure carbon.
Animal charcoal	Carbon and calcium phosphate.
Bone black	Carbon and calcium phosphate.
Drop black	Carbon and varying amount of ash.
Frankfort black	Carbon and varying amount of ash.
Graphite	Natural carbon and mineral ash.
Hydrocarbon black	Very nearly pure carbon.
Ivory black	Carbon, calcium and magnesium phosphate.
Lampblack	Very nearly pure carbon.
Mineral black	Ground slate.

GREEN PIGMENTS.

Trade Name.	Composition.
Brunswick green	Usually Prussian blue and chrome yellow on an inert base.
Chrome green	
Emerald green	Aceto-arsenite of copper.

416. ATOMIC WEIGHTS OF THE MORE COMMON ELEMENTS.

0 = 16.	Atomic Weight.	Symbol.
Aluminum	27.1	Al
Antimony	120.2	Sb
Arsenic	75.0	As
Barium	137.4	Ba
Bromine	79.96	Br
Cadmium	112.4	Cd
Calcium	40.1	Ca
Carbon	12.0	C
Chlorine	35.45	Cl
Chromium	52.1	Cr
Cobalt	59.0	Co
Copper	63.6	Cu
Hydrogen	1.008	H
Iodine	126.85	I
Iron	55.9	Fe
Lead	206.9	Pb
Magnesium	24.36	Mg
Manganese	55.0	Mn
Mercury	200.0	Hg
Molybdenum	96.0	Mo
Nitrogen	14.04	N
Oxygen	16.0	O
Phosphorus	31.0	P
Platinum	194.8	Pt
Potassium	39.15	K
Silicon	28.4	Si
Silver	107.93	Ag
Sodium	23.05	Na
Sulphur	32.06	S
Zinc	65.4	Zn

417. FACTORS FOR GRAVIMETRIC ANALYSIS.

Determined as.	Required.	Factor.
Al_2O_3	Al	0.5303
As_2S_3	As	0.6093
As_2S_3	As_2O_3	0.8043
$Mg_2As_2O_7$	As_2O_3	0.6372
$BaSO_4$	Ba	0.5885
$BaSO_4$	$PbSO_4$	1.3004
$BaSO_4$	$CaSO_4$	0.5837
$BaSO_4$	$CaSO_4 2H_2O$	0.7382
$BaSO_4$	SO_3	0.3433
$BaSO_4$	SO_2	0.2747
CaO	Ca	0.7143
CaO	$CaCO_3$	1.784
$CaCO_3$	CO_2	0.440
CaO	$CaSO_4 2H_2O$	3.0715
$CaSO_4 2H_2O$	SO_3	0.4561
CO_2	$2PbCO_3 Pb(OH)_2$	8.8068
Cr_2O_3	$PbCrO_4$	4.2288
Cr_2O_3	CrO_3	1.3137
Cr_2O_3	$PbCrO_4 PbO$	7.1438
Fe_2O_3	Fe	0.7000
K_2SO_4	K	0.4491
K_2PtCl_6	K	0.1612
K_2PtCl_6	K_2O	0.1941
$Mg_2P_2O_7$	Mg	0.2188
$Mg_2P_2O_7$	MgO	0.3624
$Mg_2P_2O_7$	$MgCO_3$	0.7575
Na_2SO_4	Na	0.3243
Na_2SO_4	Na_2O	0.4368
$PbSO_4$	Pb	0.6832
$PbSO_4$	PbO	0.7359
$PbSO_4$	Pb_3O_4	0.7536
$PbSO_4$	$2PbCO_3 Pb(OH)_2$	0.8526
$PbSO_4$	$PbCrO_4$	1.0676
$Mg_2P_2O_7$	P_2O_5	0.6376
SO_3	$PbSO_4$	3.788
Zn	$ZnSO_4$	2.478
Zn	ZnO	1.2462
$ZnSO_4$	ZnO	0.503

418. MEASURES, WEIGHTS AND TEMPERATURES.

One Imperial gallon = 277.27 cubic inches.
One wine gallon = 231.0 cubic inches.
One wine gallon = 3.7854 liters.
One wine gallon = 8.3389 pounds water at 40 C.
One quart = 57.88 cubic inches.
One quart = .9464 liter.
One liter = 1.0567 quart.
One cubic foot = 28315 cubic centimeters.
One cubic inch = 16.38 cubic centimeters.
One cubic centimeter = .061 cubic inch.
One pound Avoirdupois = 453.6 grams.
One ounce Avoirdupois = 28.35 grams.
One gram = 15.432 grains.
One inch = .0254 meter.
One foot = .3048 meter.
One yard = .91438 meter.
One meter = 39.3708 inches.

$$\text{Fahrenheit degrees} = \frac{9\,\text{C.}^\circ + 32}{5}.$$

$$\text{Centigrade degrees} = \frac{5\,(\text{F.}^\circ - 32)}{9}.$$

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