A PRACTICAL TREATISE

ON THE

MANUFACTURE OF COLORS

FOR

PAINTING.

COMPRISING

THE ORIGIN, DEFINITION, AND CLASSIFICATION OF COLORS; THE
TREATMENT OF THE RAW MATERIALS; THE BEST FORMULÆ
AND THE NEWEST PROCESSES FOR THE PREPARATION
OF EVERY DESCRIPTION OF PIGMENT, AND THE
NECESSARY APPARATUS AND DIRECTIONS
FOR ITS USE; DRYERS; THE TESTING,
APPLICATION, AND QUALITIES
OF PAINTS, ETC. ETC.

des Hêtres BY

MM. RIFFAULT, VERGNAUD, AND TOUSSAINT.

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PREFACE.

The volume here presented to the American public, derived as it is from the last and greatly improved Paris edition of the well-known work of MM. Riffault, Vergnaud, and Toussaint, edited by M. F. Malepeyre, is believed to be by far the most thorough and complete treatise upon the important subject which it considers, ever published in the English language.

It comprises some account of those pigments now known to have been used by the ancients; the principles of color as developed by Chevreul; thorough descriptions of the nature and properties of the raw materials used, and the processes and machinery for the manufacture of an immense variety of pigments; the combinations necessary in the compounding of those colors, hues, and tones which are the results of the mixture of colors; practical information as to dryers; and a variety of analyses and tests of pigments, and much other useful information.

The translator has devoted great care and attention to the faithful rendering of the production of the French authors, while the publisher has at the same time endeavored to present the book in a neat and creditable form, and both trust that their efforts will be appreciated, and that the book will meet with a rapid and extended sale as well in Great Britain as in the United States.

PHILADELPHIA, June 25, 1874.

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INTRODUCTION ON THE COLORS EMPLOYED BY THE ANCIENTS.

SEVERAL ancient writers, and especially Theophrastes, Pliny, and Vitruvius, have transmitted to us interesting data regarding the colors known in their times, and which were so skilfully employed for adorning their public and private buildings. In our time, the chemists, Sir Humphry Davy, Chaptal, and Vauquelin, and the painter, Mérimée, have analyzed these materials, and have also examined the modes of preparing and applying them. We think that it will be found useful to reproduce here a few extracts from these important researches, in order better to appreciate the progress of this branch of chemistry since the days of old.

White used by the Egyptians and Romans.—The white employed by the Egyptians is remarkably fast and well preserved. Mérimée thinks that it is simply plaster of Paris (sulphate of lime) mixed with a certain glue or mucilage, the nature of which he could not ascertain.

In certain vessels discovered in the excavations of the baths of Titus, at Rome, various pigments were found, which were analyzed by Davy, and which corresponded with those of the fresco paintings of that palace, or those of fragments of stucco work discovered in the ruins.

The same chemist ascertained that, in general, the ancient whites were soluble with effervescence in the acids, and presented the characteristics of carbonate of lime.

The whites contained in the vases of the baths of Titus, where many mixed colors were found, appeared to Davy as being of different kinds, that is, very finely pulverized chalk, another white slightly yellowish, like cream, and perfectly comminuted clay. Moreover, none of the whites examined by this chemist, whether in these baths or in any monument of Roman antiquity, contained a trace of white lead, although Pliny and Vitruvius, especially the latter, claim that white lead was a commonly used paint, produced by the action of vinegar upon lead.

In all Egyptian pictures, whether made upon wood or canvas, the priming coat is always some kind of a white, and the colors applied afterwards, although opaque, are somewhat wanting in depth and brightness, on account of a certain transparency in the groundwork. What was the nature of the size employed, is an important question, because these pictures were not cracked, as are so many of our own old ones. Egypt possesses *mimosa* trees, which produce a gum, and as gelatin glue was known, the colors may have been sized with these two substances; but Mérimée supposes that a more supple material, like gum tragacanth, or any similar mucilage, was preferred.

With what tools were these pigments applied? The answer to this question seems obvious, since the invention of the brush or pencil is so natural, that it cannot have escaped the attention of the Egyptians.

Blacks and Browns.—Davy found in several places fragments of stucco painted black. By several tests, he ascertained that acids and alkalies were without action upon the colors, but that they burned with nitre, and had all the properties of a pure carbonaceous substance.

In the vessels filled with mixed paints, which we have already mentioned, Davy found no black, but various kinds of browns—one had the color of tobacco; another was a dark red-brown; and a third was a dark olive-brown. The former two were ochres which, very likely, had been calcined at various degrees; the third yielded oxides of manganese and of iron, and produced vapors of chlorine when treated by hydrochloric acid.

"All the ancient authors," says Davy, "describe the artificial blacks of Greece, or Rome, as carbonaceous substances, manufactured from burned resins, giving a kind of lampblack, or from the calcination of ordinary soot, or of wine lees. Pliny asserts that a natural fossil black is found, and also another prepared from an earth having the color of sulphur." It is probable, according to Davy, that these substances are manganese and iron ores.

"It is evident that the ancients were cognizant of manganese ores, from their paintings on glass." Davy examined two samples of purple glass of Roman manufacture; and both were colored with manganese oxide. Pliny speaks of various brown ochres, one especially, which he calls *cicerculum*, coming from Africa, and which probably contains manganese. Theophrastes mentions a mineral substance which takes fire when oil is poured upon it, a property which, according to Davy, belongs to no other actually known mineral substance, except a manganese ore found in Derbyshire.

The browns, in the pictures of the baths of Livia, and of the Aldobrandini Wedding, are considered by Davy as mixtures of ochres with blacks. Those of the Aldobrandini Wedding yield iron when treated by hydrochloric acid, but the dark shades are unacted upon by the acid or alkaline solutions.

Yellows.—Davy discovered, in a room of the baths of Titus, a large earthenware pot, holding a large quantity of yellow paint, which, after analysis, was found to be a mixture of yellow ochre and chalk (carbonate of lime). There were in the same vessel three different kinds of yellow, two of which were yellow ochre mixed with variable proportions of chalk, and the third one yellow ochre mixed with red lead.

The yellow most esteemed by the ancients was the ochre of Athens. Vitruvius asserts that at his epoch the mine was abandoned.

According to Davy, the ancients possessed two other paints which were yellow or orange—the *auri pigmentum*, the color of which resembles gold, and which appears to be orpiment (sulphide of arsenic); and a pale sandaraca, which Pliny asserts to be found in gold and arsenic veins, and which was imitated at Rome by a partial calcination of white lead. From what Pliny says, Davy infers that the lightest kind of orpiment resembles sandaraca, and that another paint, called *sandaraca* by the Romans, was of a bright yellow, like that of the beak of the blackbird.

Davy saw no example of the use of orpiment in old fresco paintings. A deep yellow, somewhat orange, and which covered a piece of stucco work, was a mixture of litharge and red lead. This chemist considers that it is very probable that the ancients employed several lead colors, such as massicot (litharge), white and red leads.

The yellows of the Aldobrandini Wedding are entirely ochres. Davy also examined the colors of a pretty painting upon the walls of a house of Pompeii, and ascertained that they were made of yellow and red ochres.

An examination of the Egyptian collection of Passalaqua, made by a commission of celebrated French chemists, under the direction of Mérimée, demonstrated the fact that among the colors employed by the Egyptians there are two kinds of yellow; one, and the most usual, is nothing else than a light yellow ochre abundantly found in the vicinity of beds of iron ore. The other, lighter and brighter, was a sulphide of arsenic (orpiment). This latter substance may be produced artificially, but, as it is also found as a mineral, it is probable that it has been employed in this state.

Red used by the Egyptians.—The red employed in the fine collection of Passalaqua is, the greater part of it, a red ochre obtained by the calcination of yellow ochre. Vitruvius asserts that a fine red ochre was obtained from Egypt.

It is not improbable that vermilion may have been employed in some places. Cinnabar was known in India from the earliest ages, and the Egyptians may have obtained it by trade.

Red employed by the Greeks and Romans.—Among the substances contained in a large earthenware vase filled with colors mixed with clay and lime, and found in an open room of the baths of Titus, Davy found different kinds of reds. One was bright, and with an orange tinge; another was a pale red; and the third was purplish. The first one, on exposure to the heat of an alcohol lamp, became darker and even fused when the blowpipe blast was applied. Further tests demonstrated that it was red lead.

The second became black by heating, but reacquired its former color on cooling. Calcination in a glass tube proved that the only volatile substance was water. Chemical tests demonstrated that it was an iron oxide.

The third sample, of a purplish-red color, was treated in the same manner, and was found to be an ochre of a different color.

After examining the fresco paintings of the baths of Titus, Davy ascertained that all of these colors had been used; the ochres especially for shadowing the pictures, and the red lead for ornamenting the borders.

The same chemist found upon the walls another red of a tone different from those found in the vase; it was brighter, and had been employed in several rooms. A small quantity of this color, scraped from the walls, and submitted to chemical tests, proved to be vermilion or cinnabar, since metallic mercury was obtained by calcination with iron filings.

The same color was also found upon several fragments of stucco work.

In the Aldobrandini Wedding all the reds are ochres. These reds, tested with acids, alkalies, and chlorine, showed neither red lead nor vermilion.

Red lead, says Davy, was known by the Greeks and Romans. According to Pliny this paint was accidentally discovered in a fire which took place at the Piræus, near Athens. White lead exposed to that fire was transformed into red lead, and the process was imitated in manufactures.

Theophrastes, Vitruvius, and Pliny describe several red earths used for painting. The earth from Sinope, that of Armenia, and African ochre produced a red paint by calcination.

Cinnabar or vermilion was called *minium* by the Romans. "Theophrastes," says Davy, "asserts that it was discovered by the Athenian Callias, in the 349th year of Rome. It was prepared by lixiviating silver ores."

Vermilion, according to Pliny, was always highly esteemed by the Romans, and its value rose so high at one time that, to prevent a further increase, the government fixed its price.

Davy found in the baths of Titus another broken vessel, filled with a light pink color, which faded by exposure to the air down to a cream color; but the unexposed parts had a lustre like carmine.

After several experiments this learned chemist ascertained that it was composed of silica, alumina, and lime, with no other mineral substance but a slight proportion of oxide of iron. Heated with oxygen in a glass tube, this color did not burn and became somewhat red. The gas escaping from the tube, being passed through lime-water, gave a precipitate of carbonate of lime. Another portion of color was also mixed with chlorate of potassa and heated in a small glass retort; when fusion took place there was a slight combustion, and the escaping gas precipitated lime-water.

It appears from these experiments that this coloring substance was a compound with some material of animal or vegetable origin. Davy put some of it upon a heated iron, and there was scarcely any smoke, but a slight smell resembling that of hydrocyanic (prussic) acid.

When caustic potassa was melted with this color, the vapors had no ammoniacal smell, although there was a light cloud in the presence of hydrochloric acid; "but," Davy says, "this is far from being an evident proof of the presence of animal matter." This chemist made a comparison of this color with the vegetable lake made from madder, and an animal lake made from cochineal at the same degree of dilution and fixed upon alumina. The madder lake, dissolved in concentrated hydrochloric acid, recovered its color by the addition of alkalies, whereas the same results did not take place with the old color. The solution of madder lake in diluted hydrochloric acid became of a fallow brown after the addition of perchloride of iron, whereas there was no change of color with the old lake. The latter and that from cochineal became darker in weak alkalies, and brighter in weak acids. There was, however, this difference; the old lake was more easily destroyed by concentrated acids. Like animal and vegetable lakes, it was immediately destroyed by a solution of chlorine.

The smoke produced by the cochineal lake, melted with caustic potassa, was greater, and there was a strong ammoniacal smell. The combustion of the madder and cochineal lakes, in oxygen, was not more vivid in appearance than that of the old lake. Davy ascertained that the loss in weight of the latter by combustion, was about one-thirtieth, made up for the greater part of the water combined with the clay of that pigment. This fact prevented Davy from determining its composition by the process of ultimate decomposition, since the results could not be certain.

From all these experiments, Davy thinks that it is impossible to determine whether this lake is of vegetable or animal origin, and he adds: "If it is of animal origin, it may be Tyrian or marine purple, and this question may possibly be solved by making comparative experiments with the purple shell."

Davy could find no instance where this lake had been employed in the old fresco paintings. The purple-reds of the baths of Titus were mixtures of red ochres and copper blues.

Grecian Purple, also called Tyrian Purple.—The *Ostrum* of the Romans, and the purple of the Greeks, was considered by these nations the finest color, and it was extracted from a shell. Vitruvius asserts that this color varied with the countries from which the shell was exported. That from the northern countries was deeper and more violet; whereas that from the southern regions was more red. This author adds that the color was obtained by beating the shell with iron tools, and that the purple liquor separated from the debris of the animal was mixed with a certain proportion of honey.

Dr. Edward Bancroft, in his experimental researches on the physical properties of fast colors, remarks: "The purple so celebrated among the ancients appears to have been discovered at Tyr, about twelve centuries before the Christian era. This dye was extracted from a univalve shell (*murex*), of which there were two species, and which were found on the shores of the Mediterranean. The throat of the animal was incised, or it was ground whole, and the mixture was allowed to digest for several days with salt and water in leaden vessels. During the last period of the Roman Empire, the use of this precious dye was restricted to a few dignitaries, under the heaviest penalties.

"In 1683, a man, who was making a living in Ireland by marking linen with a fine crimson color, extracted from a sea-shell, found out after some researches on the coasts of Sommersetshire and Wales, quantities of buccina, which gave forth a viscous and whitish liquor when bled near the head. Marks made with this liquor would, by contact with the air, become of a soft green color which, by exposure to the sun, turned by degrees to a fast and fine purple. In 1769, De Jussieu found on the western coast of France, a species of buccinum similar to the garden snail; and the following year, de Reaumur observed that on the coasts of Poitou this same shell-fish was very abundant. The same naturalist had already found, in 1736, on the shores of the Mediterranean, the *purpura*, the only species of murex which was then known. All these shell-fish furnish a liquor, which, to a greater or less extent, possesses the above-mentioned properties."

According to Pliny, the finest purple was of a dark pink, and he asserts that it was employed for imparting a finishing lustre to the sandyx, which was a compound of ochre and sandaraca calcined together, and resembling our crimson.

Blues.—This color, as bright as ultramarine, was found in the collection of Passalaqua, and is a sort of blue ash, vastly superior to that manufactured at the present time. The latter, indeed, is rapidly acted upon by heat, acids, and alkalies, and even becomes green by age; on the other hand, the Egyptian blue resists the action of all these agents, and retains its brightness after thirty centuries.

A blue color, taken from an Egyptian grave at Thebes, was analyzed by Vauquelin. This blue was quite fusible. Heated with the blowpipe upon charcoal, and with the addition of cream tartar, it gave metallic copper. The approximative result obtained by this chemist was:—

Silica	70
Lime	9
Oxide of copper	15
Oxide of iron	1
Soda and potassa	4

"I do not know," says he, "whether this color was prepared by the wet or the dry way; but it is certain that the constituent parts are thoroughly combined, since concentrated acids remove but traces of copper and lime, and nothing at all at a second treatment." Vauquelin saw a similar color produced in the bed of a copper melting furnace, at the manufactory of Romilly; the chemical composition and the tone of the blue were the same. This Egyptian blue is more than thirty centuries old, and if certain parts have been slightly altered, it is only at the surface. Theophrastes speaks of this blue color, as being manufactured at Alexandria, and having been discovered by a king. We read in Vitruvius that Vestorius, on his return to Italy, gave its composition. It was prepared at Pozzuoli, by triturating together copper filings, sand, and natron, and forming balls which were afterwards heated in a potter's oven.

Davy succeeded in making a blue color similar to that of Egypt, by strongly heating for two hours a mixture of—

Pulverized silicious stone	20
Carbonate of soda	15
Copper filings	3

"The blue prepared by this chemist," says Julia de Fontenelle, "differs from that analyzed by Vauquelin, by melting at a lower temperature than the Egyptian blue; this result appears to be due to the greater proportion of carbonate of soda."

"The blues employed by the ancients," says Davy, "are pale or dark, according as the proportion of carbonate of lime is greater or less; but when the carbonate of lime is removed by acids, they have the same body and appearance, that is to say, a highly comminuted blue powder, similar to the finest smalt and ultramarine blues. This powder is hard, retains its color at a red heat, and fuses at a higher temperature." Davy ascertained that this blue color was not altered by the acids; aqua regia, however, after a protracted boiling with it, becomes yellow, and shows the presence of copper. A certain quantity of this color was kept fused for half an hour with double its weight of hydrated potassa; the mass was of a greenish-blue, and after treatment with hydrochloric acid, gave a proportion of silica greater than three-fifths of the primitive weight. The coloring matter was easily dissolved in ammonia, imparting to the latter an intense blue color, from which Davy concludes that it was oxide of copper. The residue was a notable quantity of alumina with a small proportion of lime.

The small amount of lime found in that color did not appear to Davy sufficient to explain its fusibility; the presence of an alkali was therefore suspected, and after the proper treatment, a residue of sulphate of soda was obtained. This was a proof that the color was a frit, colored by oxide of copper. According to Davy, there appears to be little doubt about this blue being that described by Theophrastes.

Pliny mentions other kinds of blues, which he calls sands (*arenæ*), and which were mined in Egypt, Scythia, and Cyprus. Davy believes that they were various preparations of lapislazuli, and the blue carbonates or arseniates of copper.

Pliny and Vitruvius speak of the Indian blue, the former stating that it was combustible. Evidently it was a kind of indigo.

Davy examined several blues from fresco paintings in the ruins of the monument of Caïus Cestius; one was of a dark indigo color, and yielded a small proportion of carbonate of copper; but the basis of the color was the above described frit. The blues of the Aldobrandini Wedding, from their resistance to the heat and acids, are believed by Davy to be compounds of Alexandria blue.

In diggings made in 1814, at Pompeii, and in the presence of Davy, a small pot was found, holding a pale blue color. It was nothing else than a mixture of lime and Alexandria frit.

M. Girardin, Professor of Chemistry at Lille, has analyzed a substance of a light blue color, found in a Gallo-Roman city of the department of Seine-Inférieure. After treatment with weak hydrochloric acid, which removed a certain proportion of carbonate of lime, the residue was of a very fine azure-blue color. The composition of the substance was as follows:—

Silica	49.4
Alumina	6.4
Lime, with traces of magnesia and iron	19.5
Soda	15.5
Oxide of copper	9.3
	100.1

After having mentioned the analyses made by Chaptal and Davy, Mr. Girardin passes to the following extract from the *Histoire de la Chimie*, by Hoëfer: "The manufacture of blue was invented at Alexandria, and Nestorius for a long time prepared it at Pozzuoli. Sand and natron (carbonate of soda) are ground together as fine as flour, and then mixed with copper filings and a little water, in order to make a paste. Balls are made with this paste, and are allowed to dry; lastly, they are put into pots, and heated in a furnace in order that they may fuse and produce a blue color." Mr. Girardin then adds:—

"This color, which is remarkable for its beauty and durability, could actually be prepared by calcining for two hours in a furnace a mixture of—

Silicious sand	60 parts
Soda ash	45 "
Copper filings	10 "

Greens.—Mérimée says that he saw no bright greens in the above-mentioned Egyptian collection. All of them being olive-green, he believed at first that they were made of a kind of chlorite, inferior in brightness to Verona earth, still in use by our painters. But he soon found out by analysis that copper was the coloring element.

A fragment, detached from the ceiling of the baths of Livia, was of a dark sea-green, like the groundwork. Davy ascertained that the coloring substance was soluble with effervescence in acids, and when precipitated and redissolved in ammonia, it imparted the blue color due to the oxide of copper. "There are," says Davy, "different tones of green employed in the baths of Titus, and also upon the fragments found in the monument of Caïus Cestius." In the vases holding mixed colors, already mentioned, Davy found three different varieties of green; one, with an olive shade, was Verona earth; the other was a pale grass-green, and had the appearance of being carbonate of copper mixed with chalk; the third was sea-green, and was a combination of copper mixed with a blue copper frit.

All of the greens examined by Davy, in the baths of Titus, were copper compounds. The green of a grapevine was so bright that it was suspected to contain arsenic, like Scheele's green, but analysis demonstrated that it was pure carbonate of copper.

Vitruvius speaks of chrysocolla as a substance found naturally in copper mines, and Pliny mentions artificial chrysocolla, made with a clay found in proximity to metallic veins. This clay was probably impregnated with copper, and Davy believes that the natural chrysocolla was a carbonate of copper, whereas the artificial chrysocolla was clay impregnated with sulphate of copper, and rendered green by some yellow substance.

Davy thinks that the name of chrysocolla is derived from the green powder employed by goldsmiths, having carbonate of copper as a component part.

Among the substances found in the baths of Titus, some were of a grass-green color. Davy at first thought that they were specimens of natural chrysocolla, but he afterwards ascertained that they were carbonate of copper. There were also round nodules of the red sub-oxide of copper, which, it is surmised, were due to nails or small plates of copper converted into oxide and carbonate, by the action of the air during several centuries.

According to Theophrastes, the ancients were well acquainted with verdigris. Vitruvius speaks of it as a color, and it is likely that many ancient greens which are now carbonates, were primitively employed in the form of acetates.

The ancients had glass of a very handsome dark green color. Davy ascertained that they were colored by the oxide of copper; but it does not appear that such glasses were powdered and then used as paints.

All the greens of the Aldobrandini Wedding were shown by Davy to be derived from copper.

In March, 1809, Chaptal reported to the Academy of Science the results of his examination of seven samples of paints found at Pompeii, in a color store.

The first of these colors was a natural product, a greenish and soapy clay, such as is found in several countries. This color appeared to Chaptal as being analogous to Verona earth.

Number two was a fine yellow ochre, freed by washing from all the foreign substances impairing either its purity or its fineness. Since this substance becomes red by calcination at a moderate heat, its yellow color, which was fully preserved, seems to Chaptal an additional proof that the ashes which buried Pompeii were but moderately hot.

Number three was a brown-red, similar to that employed at the present time for coarse paintings upon barrels and doors, windows, etc. This color is produced by the calcination of yellow ochre.

Number four was a very light, white, and close-grained pumice-stone.

The three other samples were compound colors, which Chaptal was obliged to analyze, in order to arrive at their constituent parts.

Number five was an intense blue, in small fragments of equal size and shape. The exterior was lighter than the inside, the color of which was deeper and brighter than the finest blue ashes.

This color produces but a slight effervescence with hydrochloric, nitric, and sulphuric acids; it even becomes brighter, and chlorine has no effect upon it. There is, therefore, no similarity, according to Chaptal, to ultramarine blue, since the latter is destroyed by the four above-named reagents, as has been observed by Clement and Desormes.

Ammonia has no action upon it. Heated with a blowpipe, it darkens and forms a reddish-brown frit. It colors borax a greenish-blue. Treated with potassa upon a platinum support, it produces a greenish frit, which becomes brown and then copper-colored. This frit is partly soluble in water; hydrochloric acid, poured into the solution, produces a gelatinous precipitate. Oxalate of ammonia gives another precipitate with the separated liquor.

Nitric acid dissolves with effervescence the residue unacted upon by the alkali. The solution is green, and gives with ammonia a precipitate which is redissolved by an excess of the reagent; the liquor is then blue.

"This color," says Chaptal, "appears, therefore, as a compound of oxide of copper, lime, and alumina; it contains the elements of blue ashes, but its chemical properties are different. It appears to be not a precipitate but a frit, that is to say, the beginning of a vitrification."

It appears that the process by which the ancients obtained that color, is lost to us. All that we know is that such a blue was employed centuries before Pompeii was buried in ashes. "Descotil," adds Chaptal, "has observed a bright blue with a vitreous lustre upon the hieroglyphic paintings on an Egyptian monument, and he ascertained that the color was due to copper.

"From its component parts, that color may be compared with our modern blue ashes; but in regard to usefulness, we may substitute for it the ultramarine and azure blues."

Number six is a light blue sand, mixed with a few whitish granules. Chemical tests demonstrated the presence of the same substances found in the preceding number. "We may," says Chaptal, "consider it as a similar compound with greater proportions of silica and alumina."

The color of number seven is a handsome pink. The material is smooth and is reduced to an impalpable powder between the fingers, coloring the skin a pretty carnation pink. By heat this color blackens, and lastly turns white, without any sensible smell of ammonia. This color is soluble in hydrochloric acid with a slight effervescence, and ammonia produces in the solution a flocculent precipitate entirely soluble in potassa. An infusion of gall-nuts, and the hydrosulphate of ammonia fail to show the presence of any metal.

We may, according to Chaptal, consider this pink color as a true lake, the coloring principle of which is absorbed by alumina. Its properties, shade, and the nature of its coloring principle render it almost entirely analogous with madder lake. The preservation of this lake for nineteen centuries, without being scarcely at all altered, is a wonderful phenomenon for chemists.

Such, says Chaptal, is the nature of the seven colors which were submitted to him, and they seem to have been especially intended for painting. Nevertheless, he observes that if we examine the varnish or glaze of Roman potteries, the debris of which are so plentiful wherever the armies of Rome established themselves, we can easily believe that most of these coloring earths could also have been employed for glazing those potteries.

The azure blue, the red and yellow ochres, and the blacks, are colors which, according to Davy, do not seem to have been altered at all in the fresco paintings. The vermilion is darker than the cinnabar of Holland, and the lustre of the red lead is inferior to that sold at the present time. The greens are generally dull.

"The principle of the composition of the Alexandria frit," adds Davy, "is perfect, *i. e.*, to incorporate the color in a composition resembling stone, in order to prevent the disengagement of any elastic fluid, or the decomposing action of the atmosphere. It is a kind of artificial lapis-lazuli, the coloring substance of which is thoroughly combined with a very hard silicious stone.

"It is likely that other colored frits could be made, and it would be worth while to try whether a fine purple, from gold oxide, could not be rendered useful for painting, by incorporating it with a glass.

"When frits cannot be employed, the experience of seventeen centuries demonstrates that the best colors are metallic combinations, insoluble in water, and saturated with oxygen or some acid substance. In red ochres, the oxide of iron is saturated with oxygen; in the yellow ochres, the metal is combined with oxygen, and sometimes with carbonic acid. These colors have remained unchanged. The carbonates of copper, which contain an oxide and an acid, have been but slightly altered."

Several parts of the figures and ornaments on the outside of the baths of Titus, present only traces of ochreous colors, and Davy thought it likely that vegetable, such as indigo, or animal colors, or different colored clays, had been employed.

To sum up, the most minute investigations, and the most thorough examinations of ancient monuments, have revealed to chemists none others than white, black, yellow, brown, red, blue, and green colors.

CHAPTER I.

ORIGIN, DEFINITION, AND CLASSIFICATION OF COLORS.

SECTION I.

ORIGIN OF COLORS.

THE decomposition of a ray of light furnishes seven distinct colors—*violet*, *indigo*, *blue*, *green*, *yellow*, *orange*, and *red*, which are generally called the *normal colors*. We may, however, say that *blue*, *yellow*, and *red* are really the only primary colors, since they are sufficient to reproduce all the others. *White* is the reunion of the seven colors, or the light of a solar ray; and *black* is the entire absence of this light.

The whites employed in painting are not a mixture of all the colors; they are natural or chemical compounds, which reflect light without decomposing it as other pigments do. The blacks absorb and prevent the luminous intensity of the other colors.

In general, the pure color of a substance is that of the color of the *prismatic spectrum* which it reflects to our eyes. A blue substance reflects blue rays only, and absorbs all others. A yellow body reflects but yellow rays; a red body reflects but red rays, etc. A white substance reflects all the rays of the spectrum, and it is their confused reunion with the same degree of intensity that appears white to our eyes. A black substance absorbs all the colors of the spectrum and reflects none.

The combination of the seven colors of the prismatic spectrum produces hues which can be varied *ad infinitum*, by the proper mixture of pigments. These hues are often called *secondary colors* in contradistinction with the *normal colors* of the spectrum.

The coloring substances employed for painting are either natural or artificial; but, as they are generally too light, they are mixed with white lead, which imparts to them body and durability.

The admixture of white with these colors renders them more luminous by diminishing the intensity of their pure color. On the other hand, black renders the other colors less luminous by a kind of absorption, without sensibly altering their specific character.

The effects resulting from the mixture of colors with blacks or whites, are totally different from those due to the mixture of colors together. This should be remembered by the painter, for it is almost impossible to obtain bright hues with an admixture of black. It has even been observed that the grays obtained by the combination of black and white, are not so fine and advantageous as the gray shades resulting from the combination of the primary colors.

We shall not, in this place, tarry any longer on the innumerable phenomena of the art of coloring, since we shall return to them when speaking of the *manufacture of colors*, which requires a thorough knowledge of the coloring substances, whether natural or artificial, and of the manner of using them. Without insisting more than is necessary upon the systematic division of normal or secondary colors, whether natural or artificial, we shall proceed to fully examine the various processes for extracting and purifying, or manufacturing, all the colors or pigments for painting. These colors are: the *whites*, *blues*, *yellows*, *blacks*, *reds*, and *greens ;* and in order to facilitate our researches, we shall follow the above order, and put the *oranges* and *violets* after the reds, and the *browns* with the blacks. As for the combinations necessary to arrive at a given hue or tone, we shall state the general principles, necessary in the majority of cases, and sufficient to obtain an infinite variety of hues and tones.

SECTION II.

DETERMINATION AND DEFINITION OF COLORS.

The study of colors, in regard to their nature and their reactions upon each other, is highly interesting. We are indebted to M. Chevreul for a new method and nomenclature, which, sooner or later, will prevail in the arts, and which is based upon the *chromatic circles* invented by this learned chemist.

In this method, all the colors are derived from invariable types or standards, disposed in a certain order comprising the hemispherical chromatic construction.

We know that every color, whatever be its nature, is either simple or compound, luminous or sombre, that is, *pure* or *broken*. Here is the mode, by means of the hemispherical chromatic construction, of arriving at the comparison and determination of colors or of their modifications :—

Let us suppose a circle, divided into three equal parts, by three radii; at the end of any one of these radii we write the word *red ;* at the extremity of the other radius on the right, we write *yellow ;* and at the end of the other radius *blue*. We then divide each of these intervals by other radii, termed *orange*, between the red and the yellow; *green* between the yellow and the blue, and *violet* between the red and the blue. Still subdividing each of these ten divisions, we have the *orange-red*, the *orange-yellow*, the *green-yellow*, the *green-blue*, the *violet-blue*, and the *violet-red*. We then divide each interval into six equal parts, and fill the first one, from the radius "red," for instance, with red, and the other five with proper mixtures of red and yellow, in such a manner that the change in hue is gradual. These five spaces are called: first red, second red, third red, fourth red, and fifth red. We operate in the same manner with all the other colors.

The primitive circle is, therefore, subdivided into seventy-two equal angular parts, each of them having a name which does not change. We understand that any simple or compound color, but pure, *i. e.*, without admixture of gray, must correspond with one of the seventy-two primitive types or standards, or be found between two consecutive types. But the latter case seldom happens, and it is always possible to interpolate by one-half, one-third, one-quarter, etc.

The broken colors are determined in the same manner, by means of types or standards. Indeed, let us suppose that a quadrant is placed perpendicular to the plan of each color of the first circle, and that the quadrant is divided into ten equal parts. Each section will receive the color modified in tone, the first by $\frac{1}{10}$ of black, the second by $\frac{2}{10}$ of black, and so on, until the tenth contains $\frac{10}{10}$, that is to say, pure black.

In practice, the hemispherical chromatic construction is reduced to ten chromatic circles. The first contains the pure colors; the second the chromatic gamuts, or scales, broken with $\frac{1}{10}$ of black; the third the colors broken with $\frac{2}{10}$ of black, and so on.

All the pure colors are not equally intense, and their coloring power is modified by white. Mr. Chevreul indicates the depth of the color by the distance from that color to the centre of the circle, in the following manner: Any one of the radii which separate the seventy-two hues, is divided into twenty-two equal parts by twenty-one equidistant points, through which the same number of circumferences are made to pass. Therefore, every angular section of the seventy-two hues is divided into twenty-two spaces. In order to fill each of these divisions, we suppose that all the hues are gradually tinted or toned in such a manner that, the centre being white, the first space is slightly tinted, the second a little more, the third still more, and so on until the twentieth, which is near the black. The first division, or white, is marked 0; the last is black, and is marked 21. The whole graduation is a *gamut*, or *scale*, of which there are seventy-two in the whole circle. The parts of this gamut are called *tones*. The *first tone* is that comprised between the first and second circumferences; the *second tone* is that between the second and third circumferences, and so on.

The color of many chemical products and coloring substances is often an indication of their purity, and it is therefore necessary to define well their coloration, and to fix it between stated limits so that but slight variations should be allowed.

We shall add that a manufacturer of Paris, Mr. Digeon, has undertaken to provide the public by chromo-engravings, with the chromatic circles of Mr. Chevreul, and that he has succeeded perfectly well in this work, which requires both skill and patience. The series of these circles is cheap enough, and should be found in the shop of every painter or manufacturer of colors.

Since Mr. Chevreul has published his fundamental ideas upon the definition and the manner of naming colors, he has communicated to the Academy of Sciences several new details, which better express their nature and applications.

"The arrangement," says he, "described in my work on the Laws of the Simultaneous Contrast of Colors, under the name of the hemispherical chromatic construction, comprises upon a circular plane 72 distinct colors, which I call a *pure gamut.* Each gamut comprises 20 tones of the same color, the intensity of which increases from the centre, which is white, to the circumference, outside of which the normal black is supposed to be. The first 10 tones, at least, of each of the 72 gamuts of the circle, contain but *primary* colors, such as red, blue, and yellow, or *binary* colors, so called because they are compounds of two primaries. These first 10 tones, at least, being without black, are called *pure tones*, and are characteristic of the *chromatic circle* of 72 gamuts, just mentioned, and which I call No. 1, as will be explained further on. 12 gamuts have the following names: *red*, *orange-red*, *orange*, *orange-yellow*, *yellow*, *yellow-green*, *green*, *green-blue*, *blue*, *blue-violet*, *violet*, *violet-red;* and 60 gamuts are by series of five, between two of the above-mentioned gamuts. The series or interpolated gamuts are numbered 1, 2, 3, 4, 5, to which is added the name of the preceding gamut, in the order mentioned. For instance, the gamuts comprised between the red and orange-red are, 1st red, 2d red, 3d red, 4th red, and 5th red, and so on.

"But are these 1440 hues and tones, belonging to 72 gamuts, sufficient to denominate all colors? Evidently not. We now have to demonstrate how the *quadrant* of the hemispherical chromatic construction completes the modification of all the tones of the chromatic circle by the addition of black. The colors are rendered gray, or *broken*, not only for the first 10 tones, at least, without black, belonging to the 72 gamuts, or scales, of the circular plan, but also for the other tones already broken.

"The quadrant being supposed mobile upon its axis, and perpendicular to the centre of the circular plan, describes during its rotation, a hemisphere, which comprises all the modifications possible by the mixture with black of the 20 tones of each of the 72 gamuts. In order to understand, let us make the quadrant coincident with one of the gamuts of the circular plan, the red for instance. The quadrant is divided by ten equidistant radii, including the axis, and the latter is also divided into 20 equal parts for the 20 tones of graduated mixtures of white and black corresponding to the 20 tones of the red gamut of the circular plan. Each of the spaces formed by the 9 other radii of the quadrant, comprises 1 gamut of 20 tones of red shaded with black, the latter being increased uniformly from the red gamut shaded with black of the circular plan to the axial gamut of normal gray. We shall then have 9 gamuts of broken red thus made: 1st red, $\frac{9}{10} + \frac{1}{10}$ black; 2d red, $\frac{8}{10} + \frac{2}{10}$ black; 3d red, $\frac{7}{10} + \frac{3}{10}$ black; 4th red, $\frac{6}{10} + \frac{4}{10}$ black; 5th red, $\frac{5}{10} + \frac{5}{10}$ black; 6th red, $\frac{4}{10} + \frac{6}{10}$ black; 7th red, $\frac{3}{10} + \frac{7}{10}$ black; 8th red, $\frac{2}{10} + \frac{8}{10}$ black;

9th red, $\frac{1}{10} + \frac{9}{10}$ black. What is said about the red can be applied to the 71 other gamuts of the circular plan.

"Thus, for each gamut of the circular plan, there are 9 gamuts of the color, broken in all its tones by quantities of black, increasing regularly (to the eye) from the circular plan to the axis of the quadrant. The hemispherical chromatic construction therefore comprises—

"I. 72 gamuts, said to be *pure*, because the first 10 tones, at least, of each of them contain no black.

"II. 72 gamuts, said to be *broken*, because their first 10 tones, at least, contain black.

"These 72 broken gamuts comprise 12,960 tones.

"III. Lastly, by adding the 20 tones of the graduated normal black, we have—

72 gamuts, each with 20 tones	=	1,440 tones
648 gamuts broken in the 20 tones	=	12,960 "
1 gamut of normal grays	=	20 "
		14,420 "

"Let us suppose that the color of any substance corresponds to 11 tones of the gamut 3 red broken by $\frac{3}{10}$, we shall write: 3d red, 11 tones, $\frac{3}{10}$.

"Now, we will understand that if the 72 gamuts broken by $\frac{1}{10}$ of black are put in a circle, and the 72 gamuts broken by $\frac{2}{10}$ of black are put in another circle, and so on, we shall have 9 circles of broken colors. By adding to them the first circle containing the first 10 pure tones, at least, we shall have 10 chromatic circles, and the broken circles will be numbered Nos. 2, 3, 4, 5, 6, 7, 8, 9, and 10.

"Up to the present time, the manufacture of the Gobelins has produced but 1440 tones of the first chromatic circle, and 72 tenth tones of the 648 broken gamuts.

"On the other hand, a skilful artist, Mr. Digeon, has produced, cheap enough for the trade, colored plates comprising the 10 tones of the 10 chromatic circles. He has also, by means of a prism of bisulphide of carbon, and conformably to the rays of Fraunhofer, reproduced the position of 15 standard colors corresponding to 15 standard colors of the first chromatic circle. In this manner it will always be possible to find these types again, and to interpolate afterwards the other colors of that first circle.

"Lastly, Mr. Digeon has made three plates which show to the eyes—

"I. How a color, blue for instance, which between the limits of white, 0 color, up to black, representing 21 tones, may give 20 distinct tones by one of my established rules.

"II. How a color and its hues, by going from red to yellow, from yellow to blue, and from blue to red, may, according to the same rule, give 72 gamuts of distinct colors.

"I set great stress on what I have just said (*i. e.*, the artifice by which I succeed in reducing an indefinite property, such as a given color, to well-defined types or standards constituting the 20 tones of that color, and the color in general considered as having its hues in definite types of 72 gamuts), because this method may be applied to the study of properties or relative properties which belong to various sciences, the object of which is the study and classification of bodies."

SECTION III.

PHYSICAL EFFECTS OF COLORS.

Colors of the rays of the solar spectrum.

1. Red.
2. Orange.
3. Yellow.
4. Green.
5. Blue.
6. Indigo.
7. Violet.

The reunion of the rays Red, Yellow, and Blue = White.
" " Yellow and Red = Orange.
" " Yellow and Blue = Green.
" " Red and Blue = Violet.

Since Yellow, Red, and Blue are sufficient to produce all the other colors, they have been called the *primary colors.*

The reflected colors which, being added to those absorbed, reproduce the white, are called *complementary colors.*

Absorbed Colors.	Corresponding Complementary Colors.
Green (*Blue and Yellow*)	Red
Violet (*Red and Blue*)	Yellow
Orange (*Red and Yellow*)	Blue
Red	Green (*Blue and Yellow*)
Yellow	Violet (*Red and Blue*)
Blue	Orange (*Yellow and Red*)

Mr. Chevreul calls *contrast of tone,* the modification experienced by two colors of the same nature, but of different tones, when they are contiguous one to the other.

Example.—When two bands of the same color, but of different intensity, are placed parallel and contiguous to each other, they are modified in their tones, which are no longer the same as when they were viewed separately, or at a certain distance from each other. The general observed phenomenon is this: the color of the two bands is entirely changed at the line of contact, and that band with the less depth of tone appears still lighter, but not uniformly so. The portions nearest the line of contact are the lightest, and the tone goes on increasing in depth up to a certain place, where the band retains its natural color. On the other hand, the darker band is modified in another manner: the portions nearest the line of contact are darkest, and the tone goes on decreasing in depth up to a certain place, where the band reacquires its natural color.

When two stripes of different colors, but sensibly equal in tone, are parallel, and in contiguity, their colors produce upon the eye an effect different from that felt if they are seen separately, or at a certain distance from each other. Each one absorbs a certain number of rays, and reflects the complementary ones, which, reacting one upon the other, modify the examined color. This optical phenomenon is called by Mr. Chevreul *contrast of colors.*

Examples :—

Juxtaposited Colors.	Corresponding Complementary Colors.	Modification by Contrast.
Orange.	Blue	= Reddish-Orange.
Green.	Red	= Bluish-Green.
Orange.	Blue	= Orange changing to Yellow.
Indigo.	Orange-Yellow	= Indigo changing to Blue.
Green.	Red	= Green changing to Orange-Yellow.
Indigo.	Orange-Yellow	= Indigo changing to Red.
Green.	Red	= Green changing to Yellow.
Violet.	Yellow changing to Green	= Violet changing to Red.
Red.	Green	= Red changing to Orange.
Blue.	Orange	= Blue changing to Green.

Mr. Chevreul, in his celebrated work on the contrast of colors, has fully explained the meaning of *simultaneous contrast, successive contrast*, and *mixed contrast.* We advise persons desirous of gaining further information on this subject, to consult that work.

SECTION IV.

CLASSIFICATION OF COLORS.

Primary Colors.	Subdivisions.
Red . .	Deep red (*crimson, gros rouge, fine red*). Cherry-red. Rose-pink.
Yellow . .	Bouton d'or. Immortelle. Straw.
Blue . .	Bleu de France (*gros bleu*). Ultramarine (*medium blue*). Celestial blue.

Binary Colors (*pure*).	Subdivisions.
Orange (*yellow and red*) .	Deep orange. Medium orange. Light orange (*Nankeen*).
Lilac (*red and blue*) . .	Violet évêque (*deep lilac*). Medium lilac. Light lilac (*Hortensia*).
Green (*yellow and blue*) . .	Deep green (*grass-green*). Medium green (*Scheele's green*). Light green (*water-green*).

BINARY MIXED COLORS.

Orange-red,	in which	red	predominates.
Orange-yellow,	"	yellow	"
Lilac-red,	"	red	"
Lilac-blue,	"	blue	"
Greenish-yellow,	"	yellow	"
Greenish-blue,	"	blue	"

Tertiary Colors (pure).	Subdivisions.
Black (*red*, *yellow*, *and blue*) . . .	Black (*black-black*, *blue-black*, *dead black*, *bright black*). Iron-gray. Pearl-gray.

Tertiary Colors (mixed.)	Subdivisions.
Garnet (*light green and red*). . . .	Puce (flea color) or (*deep garnet*). Medium garnet. Light garnet or (*tobacco*).
Bronze (*lilac*, *blue*, *and yellow*) . . .	Bronze. Olive. Réséda.
Brown (*orange*, *red*, *and blue*) . . .	Maroon (*brown-solitaire*, *bistre*). Wood. Hazelnut (*stone-drab*).

SECTION V.

GENERAL METHOD OF PREPARING COLORS.

We cannot do better than to present to manufacturers of colors, the observations of a skilful chemist, Mr. Kletzinsky, as embodied in a memoir, the general principles of which are here reproduced.

A fact which appears to be beyond doubt, says Mr. Kletzinsky, is that, in the chemical manufacture of colors, the wet way presents many advantages over the dry way. This was long since demonstrated in the manufacture of vermilion by the wet way, that is, by precipitating a salt of oxide of mercury with a sulphur solution. The vermilion produced is much superior to all the other kinds of cinnabar obtained by sublimation or the dry way. It is physically impossible by the dry method, and by the mechanical operations of pulverizing, sifting, grinding, and even levigating (floating), to arrive at a molecular comminution equal to that obtained by the wet way, that is, by the precipitation of a coloring substance by the mixture of two limpid and pure solutions. It is also a well acknowledged fact that to the molecular grain of a pigment, that is, its degree of comminution, are due its freshness, intensity, tone, body, and facility of entering into mixtures.

Therefore, if a high degree of comminution is one of the most important conditions for artistic and house painting, it becomes still more so when we have to produce given hues by the intimate and thorough mixture of two or more colors. For instance, we desire to make a leaf-green by mixing together chrome yellow and Berlin blue; it is evident that we will obtain a good and constant green color, with the proper freshness and brightness, only by a previous thorough comminution of each separate color, and afterwards by their intimate admixture, so that the blue and yellow rays will be reflected from the same point, and will become blended and produce the green optical effect on the eyes of the observer. As such a result will evidently be reached more easily and cheaply by the wet way than by the long and tedious method of grinding, the principle of "mixeolytical" colors is entitled to our serious attention for a great many chromatic productions, and in the chemical manufacture of colors. This principle is:—

"Choose two couples of solutions in such a manner that each couple is capable by itself, when mixed, of producing a precipitate possessing all the necessary qualities of a chemical color."

Let *a*, *b* and *c*, *d* be these two couples of solutions; *a* and *b*, by their admixture, produce the blue; and *c* and *d*, under the same circumstances, result in yellow. If now, with the proper chemical knowledge, we choose such solutions that a and c, b and d, be mixed without decomposition, or production of indesirable precipitates, we have realized the *mixeolytical* principle, since the mixture of the double solution a c with the double solution b d, will immediately give the precipitate of the new mixeolytical green color. Since a thorough solution is perfectly homogeneous, and all its parts have the same density and give the same yield, we immediately see that the precipitated pigment will have a fineness and a uniformity of hue and tone which cannot be attained by colors prepared by mixing and grinding.

The following mixtures are examples of the above mentioned method :—

1.

Mixed double solution (a, c).		Mixed double solution (b, d).
Neutral chromate of potassa,	*Yellow*	Acetate of lead.
Yellow prussiate of potassa,	*Blue*	Acetate of iron.

Resulting in a DEEP GREEN color, which may be brightened with nitric acid.

2.

Sulphuretted hydrogen solution	*Yellow*	Nitrate of cadmium.
Yellow prussiate of potassa,	*Blue*	Nitrate of iron.

Together, a SCHEELE'S GREEN, which is not poisonous.

3.

Phosphate of soda (in excess)	*Blue*	Nitrate of copper (in excess).
Neutral chromate of potassa,	*Yellow*	Nitrate of lead.

Together, a LIGHT LEAF-GREEN.

4.

Yellow prussiate of potassa,	*Blue.*	Perchloride of iron.
Chloride of barium	*White*	Sulphate of ammonia.

Together, a CELESTIAL OR MARIE-LOUISE BLUE.

5.

Sulphuretted hydrogen (solution).	*Brown*	Chloride of tin.
Yellow prussiate of potassa,	*Blue*	Perchloride of iron.

Together, an OLIVE GREEN, which may be brightened with very diluted nitric acid.

6.

Sulphuretted hydrogen (solution).	*Brown*	Chloride of tin.
Yellow prussiate of potassa,	*Cassel's red.*	Sulphate of copper.

Together, a DEEP BISTRE color, having a good body.

These few examples are sufficient to give an idea of the almost boundless series of permutations with mixeolytical combinations. It is not only possible to multiply the mixtures, but the relative proportions of the solutions may also be varied to produce as many tones and hues of the same color as may be desired, and that much more easily than in the usual method of grinding a mixture of two colors.

It is well understood that experiments should be made with titrated solutions, *i. e.*, those the composition and yield of which are well known, and also with graduated vessels of a known volume. It is the only way of reproducing in the course of manufacture a color or shade which is satisfactory, and which may previously have been obtained by a chance hit, or otherwise.

CHAPTER II.

MANUFACTURE OF COLORS.

SECTION I.

WHITE COLORS.

We have previously explained what is the origin of colors, how they are determined and classified, and what is their general mode of preparation. We have now to examine the processes employed in the preparation of every one of them, and we shall begin with the white colors which are employed not only directly as pigments, but also for lightening a great many other colors.

For a long time, chalk white and white lead were almost the only whites in use; but, of late, the painter's palette has become furnished with several new white pigments, such as zinc-white, baryta-white, or blanc-fixe, which, from their peculiar properties, have been found very advantageous for house painting. We shall describe their manufacture very carefully, without, however, neglecting the description of the more recent processes for the preparation of white lead, processes which are very varied, and many of which are now in use.

§ 1. *Whites with lime basis.*

1st. *Carbonate of lime.*

The *chalk whites*, or carbonates of lime, are quite abundant; they form large deposits in England, and in France, especially near Rouen, and at Meudon, and Bougival, near Paris. This white is sometimes yellowish, but oftener grayish or entirely white. Its fracture is earthy, fine, and without any polish. It is soft, without greasy feeling, leaves its marks, and adheres to the tongue. Chalk contains a small proportion of silica, sometimes magnesia, and about 2 per cent. of clay. There is iron in some samples.

Prepared chalk is called Spanish white, or white of Bougival, Champagne, or Troyes, according to the place of its manufacture. It is prepared as follows:—

After picking out the coarser impurities, it is ground in a mill and formed into rolls, in which shape it is found in the trade. For painting purposes it is further purified by stirring in clear water, allowing it to settle, and decanting the first water, which is generally yellow and dirty. The washing is repeated, and the chalk is floated out into another vessel, after passing through a silk sieve. After settling, the water is decanted, and the pasty white residue is formed into cylindrical rolls 10 to 12 centimetres in height, and 5 to 6 in diameter. These are allowed to harden and dry in the air, and are then ready for painting, whitewashing ceilings, and for distemper painting with size.

Mr. Lazé thinks that if chalk whites are not substituted for white lead, it is due to the presence in the former of a certain proportion of sand, which it is difficult to remove. Better results are obtained by sifting than by simple washing. A well-prepared chalk-white, mixed with a little blue, and a dryer, may be employed for oil painting.

2d. *White of sulphate of lime.*

The natural sulphate of lime, also called gypsum, or crude plaster of Paris, is chosen as pure and white as possible, and then finely powdered and sifted. This white is employed for the grounds of paper-hangings, and also with size for house painting. Some manufacturers adulterate zinc-white with it.

§ 2. *Whites with lead basis.*

The finest ceruse whites, or white leads, are those manufactured at Krems, or Kremnitz (Hungary). But, as their preparation requires numerous operations, involving great labor, and much time, chemists have endeavored, by new and more rapid, simple, and cheap processes, to diminish the time and cost of manufacture, without sensibly altering the quality of the products.

In the order of their qualities, the white leads by the Holland process come after those of Krems, and next those of Clichy, which will be mentioned further on.

Before describing various processes of this manufacture, the products of which are the basis of nearly all pigments for house and artistic paintings, we shall present a few general observations on the preparation of white lead which are due to Mr. Benson, a skilful chemist and manufacturer, and which may be applied to any kind of white lead, and are therefore useful to manufacturers.

The white lead manufactured by the Clichy process, that is, by the precipitation of a basic acetate of lead with carbonic acid, is different from that of Kremnitz. And, although the manufacture has been largely extended, we believe that the processes could be improved and rendered cheaper.

At the same time, we agree with practical painters, that the Clichy or chemical white lead is less dense and possesses less body than the Kremnitz white.

This fact, demonstrated by experience, notwithstanding a few contradictions, has caused several chemists and manufacturers to go back to the Kremnitz process, and to try at the same time to diminish the length of the operation. Many have been the attempts to employ the oxides of lead abundantly found in the trade, and to do away with the employment of boxes which requires so much time for the simultaneous oxidization and carbonatation of the lead.

Of litharge, Mr. Benson remarks that it is seldom specially manufactured except for certain wants in the arts, and that it is a secondary and abundant product obtained in all the lead works which extract silver from lead.

The quantity of litharge produced in England, where a great many lead mines are in active operation, is much in excess of the consumption in the arts. It is therefore necessary to reduce to the metallic state that excess of litharge, notwithstanding a loss of 7 per cent. of its metal, either by sublimation or by combination with the earthy substances of the fuel with which it is in contact during the operation.

Litharge being a protoxide of lead, it was believed that in order to transform it into white lead, it was sufficient to combine it with carbonic acid. It is a mistake which has given birth to many erroneous processes.

In all of these processes the litharge is transformed into a basic salt, which is precipitated in the form of a carbonate by a stream of carbonic acid. The precipitate thus obtained is white, but the painters who first used it said that it was not white lead. On the other hand, several chemists having found in it, by analysis, a correct relation between the oxide of lead and the carbonic acid, thought that the painters were prejudiced.

Dr. Ure appears to have been among the first to ascertain the difference between white lead and the precipitated carbonates. White lead is anhydrous, amorphous, and opaque in oil; whereas Dr. Ure found out by microscopic observations that the precipitated carbonate was partly crystalline and translucent.

There is a remedy for this inconvenience which appears to have been already in use for some time. The mode of operation either for the crystalline carbonate or the amorphous one is after all the same. In both cases the lead is converted into a basic acetate, decomposed afterwards by carbonic acid; but for the crystalline carbonate the operation is modified by the pressure of the liquid in which it takes place.

In one process the carbonate is deposited in a solution, in the other the molecules remain all the time in the solid state and have no opportunity of being symmetrically grouped.

Therefore, in order to produce an amorphous carbonate or white lead from litharge, the oxide of lead should be combined with such a small proportion of acetic acid that the resulting basic acetate is insoluble, and there should be just enough dampness to allow of the action of the carbonic acid.

The process becomes then a counterpart of that in general use, with the exception that in this case the lead is in the oxide state, whereas in the ordinary method the oxidization and carbonatation proceed simultaneously.

This process is actually practised on a very large scale in a manufactory near Birmingham. The proportion of acetic acid employed is less than $\frac{1}{300}$ of the weight of the litharge, which should feel simply moist to the hand.

The combustion of coke gives a cheap supply of carbonic acid, and a powerful stirring machinery is employed to hasten the operation by constantly presenting fresh surfaces to the action of the gas.

The result is that the operation is finished in as many days as months were required by the old methods; that the product is of a purer white, more opaque and with more body, and that in every respect it is at least equal to the white lead of the trade.

Before describing this process more completely, it is important to state certain facts which are not sufficiently known.

It is quite remarkable that the protoxide of lead known under the name of massicot, and that called litharge, behave differently when they are brought up nearly to a red heat. The massicot absorbs oxygen rapidly and becomes the ordinary red lead of the trade; on the contrary, this absorption is very slow, and sometimes fails entirely, with litharge. On the other hand, should litharge and massicot be wet with diluted acetic acid and exposed to a stream of carbonic acid, the litharge will be converted into carbonate even before the massicot is acted upon.

Another fact is, that white lead and oil combine with such energy, that if linseed oil is poured upon a large quantity of white lead, and the mass allowed to stand for a few hours, the temperature becomes so high that the oil is carbonized and colors the whole a dark black.

It is also not generally known that white lead destroys the coloring principle of linseed oil. If sulphate of baryta be mixed with linseed oil, and white lead with a similar proportion of the same oil, the latter will appear whiter. After allowing these two mixtures to rest for a few days, a certain proportion of oil will rise to their surface. In the first case the oil has not been modified, in the second it has become almost entirely white, and has acquired a certain degree of rancidity.

The coloring principle of the oil, as some persons might believe, is not combined with the white lead but is destroyed. Indeed, should we dissolve the lead by means of some acid, the oil is separated, and as white as that which was on the top of the mixture.

Such a transformation requires a great excess of white lead, and the precipitated carbonates are not so advantageous for painting.

Basing their operations upon the above considerations, Mr. Benson, and Mr. W. Gossage, another distinguished chemist, have established a manufacture of white lead by an improved Kremnitz process, which we shall now examine.

1st. *Kremnitz process.*

The manufacture of white lead by this improved process requires oxides of lead and acetic acid, or acetates of lead and carbonic acid.

The oxides of lead are well known and abundant in the trade. Any oxide of lead, whatever is its preparation, which may be cheaply combined with carbonic acid, is satisfactory for this process.

Among the various oxides of lead found in the trade, litharge and massicot are the best for this operation. Red lead or minium does not suit at all.

The acetic acid employed should be free from coloring substances, which would discolor the white lead and impair its value. Acetic acid, free or already combined with oxide of lead, is used. The acid, as every chemist knows, may be obtained nearly colorless by the distillation of vinegar, or by the decomposition of the acetate of lime, or of any other combination of acetic acid with earthy, alkaline, or metallic bases.

It is not necessary to reproduce in this place the manner of effecting these decompositions, which is known to every manufacturer. Moreover, such an acetic acid is at the present day a product of the chemical trade.

When acetate of lead is used, the neutral acetate or sugar of lead, and the basic solutions called *Extract of Saturn* and *Goulard's water*, are employed.

Carbonic acid may be obtained by several methods actually in use; but that which is preferred on account of its cheapness consists in collecting the gas resulting from the combustion of charcoal, coke, or anthracite.

In order to obtain a carbonic acid entirely satisfactory for the manufacture of good white lead, it is absolutely necessary that the fuels used should be entirely deprived of bituminous or volatile substances, that is to say, be nearly pure carbon with fixed substances (earths).

These materials are burned in a stove or oven, and the gases produced, which are a mixture of carbonic acid, nitrogen, and undecomposed air, are passed through a series of metallic pipes, so disposed in the air or in water, that the gases are cooled off to a moderate temperature.

In order to arrest any particles of unburt carbon, or any other substance which may injure the color of the white lead, the gases are passed through filters filled with irregular fragments of lead, such, for instance, as may be obtained by pouring the molten metal into cold water.

A small stream of water is allowed to percolate through the lead filters, which, therefore, are kept constantly wet during the passage of the gas, and aid considerably in its purification. When the presence of sulphur is suspected in the fuel employed, a small proportion of alkali is added to the water of the filters. Notwithstanding this precaution, it is better to be very particular in the choice of the fuel intended for the production of carbonic acid.

The carbonic acid already in the atmosphere could be employed for carbonating the oxide of lead, if its proportion were not so small. The operation would be so slow, that, in every respect, it is preferable to prepare carbonic acid by artificial means.

The following is the manner of manufacturing white lead with the above indicated materials:—

If the oxide of lead is in big lumps, it is necessary to grind it down to a powder, which needs not to be so very fine. Litharge seldom requires this operation, and may be employed in the state in which it is bought.

The oxide of lead is mixed with the necessary proportion of acetic acid, or acetate of lead, and sufficient water is added to make a consistent paste. This paste is spread in thin layers over trays covered with sheet lead, and these trays are disposed one on top of the other in a room for the purpose, into which enters the carbonic acid, either pure, or mixed with other gases which cannot have any bad effects upon the beauty of the product. The carbonic acid is absorbed, and combines with the oxide of lead to make *ceruse* or *white lead.*

During the operation, the absorption is aided and rendered more rapid, by stirring with rakes the layers of lead, and thus presenting fresh surfaces to the action of the carbonic acid.

If the gas is dry, or does not carry with it sufficient dampness, a certain quantity of water is added to the mixture so as to render it more ready to absorb the carbonic acid. The proper degree is easily arrived at after several trials during the operation.

As the operation progresses, the oxide of lead, which was colored, becomes white; and when all of the mixture is free from colored parts, the treatment is finished, since all of the oxide has been transformed into carbonate.

The length of the operation varies with the proportion of acetic acid or of acetate employed, the rapidity of production of carbonic acid, and the attention given in stirring and in maintaining the proper degree of dampness. With the proportions of oxide of lead, acetic acid, or acetate, given further on, and a production of carbonic acid sufficiently rapid, and the proper care, the carbonatation requires from three to six days.

It has been found economical to mix at once part of the oxide of lead with the whole of the proportion of acetic acid or of acetate, and when this oxide is very nearly transformed into carbonate, to add a new proportion of oxide without any more acetic acid or acetate of lead. This new mixture, being exposed to the action of the carbonic acid, the free oxide is very rapidly converted into carbonate. A new proportion of oxide is again added, and the operation is continued as before, and always with a proper amount of moisture.

These successive additions of oxide are repeated (without more acetic acid or acetate) until the proportion of acetic acid or of acetate is reduced to one-fourth, or even less, of that which was in the primitive mixture.

When the carbonatation is finished, the mixture is spread in a stove-room, and allowed to dry. Then it is ground in a mill with water in the ordinary manner. The ground and floated product is dried again, and is white lead for painting and all other purposes.

The carbonated mixture may be ground immediately after its removal from the trays, without drying it first; but the latter operation improves the quality of the white.

For 100 kilogrammes of oxide of lead, we employ the same weight of a solution of acetic acid which contains 23 litres of No. 24 or *proof vinegar*. When we use acetate of lead, either solid or in solution, we take of either a quantity yielding the proportion of acetic acid just mentioned.

2d. *Holland or Dutch process.*

We now pass to the details of the operations by the Holland process, with various observations and comparisons made in several large French works, by

Mr. R. Combes, and reported by him to the Academy of Sciences.

The Holland or Dutch process comprises the following operations:—

1st. Fusion and casting of the lead in sheets of variable thicknesses, or into rectangular or round grates (buckles).

2d. Alternate layers made of lead and stable manure, or spent tan. The lead is put into pots holding weak acetic acid, and remains in the beds from thirty-five to forty days when stable manure is employed, and from seventy to ninety days when spent tan is used.

3d. Successive uncovering of the layers of lead, the greater part of which has become carbonate. Separation of the white lead from the non-corroded metal. First grinding and separation of the blue lead.

4th. Grinding the white lead with water under stones.

5th. Moulding and drying the floated white lead.

6th. Grinding and sifting the dry white lead, and packing in barrels that which is to be sold powdered.

7th. The white lead which is to be made into paste with oil is not sifted, but mixed with from 7 to 10 per cent. of its weight of oil. The mixture is effected in a closed stirrer, and then passed between a series of horizontal cast-iron rollers. When the paste has become fine and homogeneous, it is received in a tank filled with water, from which it is taken and packed for sale.

I. The fusion of the lead is effected in cast-iron kettles, and no dangerous fumes are emitted unless old lead or the residues of previous operations, still covered with carbonate, are melted. In well-disposed works, the kettle is placed under a hood receiving its draft either from the chimney flue of the furnace itself, or from another stack with a good draft. The top edge of the furnace is connected with the hood by means of a metallic prism or cylinder, having doors which are open for charging the lead, or for casting into moulds the fused metal. These precautions seem to us sufficient for protecting the men from the noxious fumes. Moreover, the fusion of the lead is intermittent.

II. The forming of the layers of lead and stable manure or spent tan, presents no danger. The buckles or the thin sheets of lead rolled into spirals, are put into earthenware pots, and there supported upon two or three projections. The vinegar is at the bottom of the pot.

In one of the lead works of the department of the Seine, the lead is cast into rectangular grates, or buckles, which form layers upon pots more shallow than usual, and holding the vinegar only.

III. The separation of the white lead from the non-corroded metal, and the first dry pounding and sifting, are the most unwholesome parts of the manufacture. In nearly all of the works of Paris, the workman picks up by hand the large and slightly adhering scales of white lead, and separates the remainder by twisting and bending in every direction the non-corroded lead. This hand picking is generally done in the bed itself, and sometimes in a special room where the whole of the corroded metal is carried, in the shape it comes from the pots.

This picking, however, where the hands are constantly covered with carbonate of lead, is not the most dangerous part of the operation, because the thick scales are separated without much dust. But as the metallic lead still retains a certain quantity of white lead strongly adhering, it was formerly beaten with a wooden rammer, thus producing a fine dust, which was inhaled by the workman. This operation is therefore the most dangerous, and is now substituted in several works by mechanical means, which imperil the health of the men much less. The buckles or sheets with their still adherent white lead are put, one by one, upon an endless cloth, which carries them to an inclined hopper, from which they pass between two pairs of grooved rollers, and thence through an inclined cylindrical sieve. What passes through the holes of the sieve is received into a hopper, which delivers it into a trough on wheels. The metallic lead falls from the lower opening of the sieve into another trough. The whole of the machinery is inclosed in tight wooden partitions, the only free opening of which is that for the passage of the endless cloth. The trough filled with white lead is removed when the dust has subsided, and its contents are mixed with the scales picked up by hand.

The next dry grinding is, in the majority of cases, still effected under vertical stones, rolling upon a horizontal bed. The ground lead is then shovelled into a cylindrical metallic sieve with fine holes, and inclosed in a wooden box. The powdered white lead is collected at the bottom of the box, and the small flattened particles of metallic lead, fall from the lower end of the sieve into a special receiver. The sifted white lead is mixed with water, and thoroughly ground under mill-stones.

In several manufactories in the neighborhood of Lille, the scales of white lead are powdered between several pairs of horizontal grooved rollers. The divided substances fall upon one or several metallic sieves, and from them into hoppers which conduct them to a receiving trough, where they are moistened with a spray of water. The metallic lead falls into a separate room. The whole of the grinding rollers and sieves occupy the height of a story, and are inclosed in wooden partitions. The upper hopper is kept filled with the scales of white lead, so as to prevent the escape of dust. Moreover it may be entirely closed with a trap door. These dispositions are a great hygienic improvement on the old process of manufacture.

In those works of the department of the Seine, where the lead is cast into grates or buckles, and not into sheets, the separation of the white lead and its dry pulverization and sifting are effected by mechanical apparatus following one another, and placed in closed rooms.

The first room contains a series of three pairs of grooved rollers which separate the white lead from the non-corroded metal, and another series of three pairs of smooth rollers which grind the scales of white lead. There is an opening at each opposite extremity of the room: one for the passage of the endless cloth carrying the corroded buckles; and the other for the escape of the cleaned lead which slides upon a sheet-iron apron, perforated with holes and made to shake by machinery. These grates or buckles of metallic lead are received by one or two workmen, who put apart the thin ones for remelting, and separate and straighten those which are thick enough to go into the beds again.

The scales of white lead, separated by the grooved rollers, fall upon an endless cloth placed under the shaking apron of perforated sheet iron, and are brought upon the three pairs of smooth rollers, between which they are powdered. The powder falls upon an inclined plane, which conducts it to a pit, from which it is taken up by an endless bucket strap (inclosed in tight wooden troughs), and carried to the top of an upper room, where the metallic sieve for the separation of the blue from the white lead is. The metallic portions are received in a distinct place, and the white lead falls on to the floor of the room, from which it is removed when the dust has settled. In this operation, the men who receive the buckles of lead from the rollers, are still exposed to the dust of the white lead, and remain but a few days at that work.

To sum up: the separation of the scales of white lead, and their dry grinding and sifting, cannot be considered a wholesome manufacture anywhere, although there have been many improvements made and hygienic precautions taken in most of the works we have visited. Certain manufacturers have tried to obviate the not very great danger of picking white lead with the hand, by furnishing the men with gloves. This precaution seems to us insufficient, because gloves are often an impediment to the work, and the men will be tempted to leave them off.

In the works where the separation of the white lead from the non-corroded metal is not done by hand, there is still danger of inhaling fine white lead dust, when the thick buckles are straightened and struck with the mallet. Lastly, a very fine lead dust escapes from the rooms containing the grinding apparatus, either from the apertures for the inlet or outlet of the substances, or from the openings cut in the wooden partitions for the passage of the shafting.

The causes of danger would quite cease to exist, if the separation of the scales of white lead, their grinding and sifting, were effected under water; or, at least, if the white lead and the metallic residues were subjected to sprays of water immediately after they leave the grinding apparatus. Such is the mode of operation, as we learn from data of Mr. Le Play, in the English white lead works. There, all the metallic residues are cast anew, before returning to the beds. We call the attention of manufacturers and of the public administration to this method, which presents no serious difficulties, since it is generally practised in England. The white lead is also deprived, by washing, of certain soluble salts which may injure its purity; moreover the subsequent operation is always effected with the aid of water.

IV. The white lead is mixed with water in troughs, so as to form a soft paste which passes successively through several horizontal mill-stones before it is thoroughly comminuted. This wet grinding is absolutely without danger, since the men do not touch the white lead with their hands, but carry it in scoops or ladles.

V. In all the works which we have visited, the soft paste of white lead is poured into conical earthenware pots, which are dried in a stove room. The greater part of the water is expelled, and the blocks becoming contracted, are easily removed from the pots. Their thorough drying is finished in another, or the same, stove room.

The sides of the pots are coated with white lead, which is generally scraped off with an iron tool. This operation is performed by women or children, and is not without inconvenience. It is remedied in certain works, by washing the pots in water; but this involves more labor and expense. Part of the white lead is sold, after drying, in the shape of conical blocks, which are wrapped in paper and put into barrels, care being taken not to break them. This handling of white lead is not entirely wholesome, although, with the proper precautions, it is not dangerous.

In an establishment of the department of the Seine, the white lead is not put into pots; but the soft paste is poured upon a cloth which is then folded so as to form a square flat bag. Several such bags, separated by square wooden trays, are afterwards squeezed in a hydraulic press, which expels the greater part of the water. After unfolding the cloth, the block of white lead is cut into prisms or bricks having sufficient consistency to be carried immediately into the drying room. A small proportion of the product of these works is sold in the shape of dry prisms; but their packing in barrels is not done with the same care as with the conical blocks, because the products go to consumers sufficiently learned to know that the external shape of white lead is no proof of its good or bad quality. The bricks or prisms of white lead are compressed in the barrel by the cylinder of a hydraulic press.

VI. The greater part of the white lead in lumps requires to be ground and sifted again before it is ready for sale. This second grinding, in the majority of works, is still done with vertical stones rolling upon a stone bed. The ground stuff is shovelled into the hopper of a cylindrical silk sieve, inclosed in a wooden box, where the fine white lead falls. That which has not passed through the meshes of the sieve is collected in another box, and ground anew. The sifted white lead is removed from its box, after the dust has subsided, and packed in barrels either by shaking, or by a slight ramming.

The grinding, sifting, and packing of the dry white lead by the foregoing method, are evidently dangerous on account of the dust floating in the workshop. The inconveniences can be considerably diminished, by inclosing within wooden partitions the mill-stones and the sieve, as is practised in lead works at Lille, where the vertical stones have been replaced by horizontal ones of white marble. Each pair of stones is within a drum, on top of which is a hopper filled with the lumps of white lead, coarsely broken by means of a rotary grooved cone placed within it. The powdered material is, by centrifugal force, projected against the drum, and falls by two diametral openings into the sieve below, which is also well inclosed. In order to prevent the dust from flying during the packing, the white lead is compressed by means of a wooden disk, of nearly the same diameter as that of the barrel, and pressed downwards by a screw.

VII. The works in the neighborhood of Lille sell the greater part of their products in the shape of powder or lumps: that is, about one-third in lumps and two-thirds in powder. A manufacturer of the department of the Seine has all the apparatus necessary for grinding the white lead in oil, and seven-eighths of his production is sold as a paste holding from 7 to 9 per cent. of oil. The prisms of white lead are ground in a kind of coffee mill, which delivers a not very fine powder. The powder is then put into a horizontal cylinder, with a certain proportion of oil, and mixed by means of iron paddles fixed to the shaft running the length of the cylinder. From thence the paste passes between a series of cast-iron rollers, and becomes fine and homogeneous. More oil is added if necessary. The finished paste is kept under water in large tubs, from whence it is taken for packing.

Thus, when white lead is ground in oil in good apparatus, like those we have seen in operation, it is not necessary to grind it into a fine powder, and we avoid one of the most unwholesome operations. It is therefore highly advantageous that all the white lead (and we believe that by far the greater part of the white lead is always ground in oil) should be mixed with oil in the works themselves, instead of in many separate shops, where the men are subject to lead colics, from want of proper precautions and apparatus. It appears certain, from what we have seen in a lead works at Birmingham, and from the data of Mr. Le Play, that the English manufactories deliver the greater part of their products in the shape of a paste holding from 8 to 9 per cent of oil.* It is highly desirable that the same thing should be done in France.

In the majority of white lead works, certain hygienic precautions are required of the workmen. Thus, when they leave work, they wash their hands, arms, and faces. Soap, fuller's earth, and sometimes tubs filled with a solution of sulphide of potassium, are put at their disposal. In one of the Paris works,

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* In England, at least in several works, there are three brands of white lead paste; the first is pure white lead with from 8 to 9 per cent. of oil; the other two qualities contain sulphate of baryta in the proportions of about 15 and 25 per cent.

tubs for sulphuretted baths are placed in a room near the boilers which furnish the necessary steam.

The men are alternately put to the unwholesome parts of the work, and do not remain long there. A cloak-room where the men leave their working clothes after work, exists in several factories. Nearly everywhere they receive gratuitously the first cares of a physician who is paid by the manufacturer.

The work-rooms are generally large and well ventilated, especially where the dry white lead is ground and sifted. However, the walls and the shafting are covered with white lead dust, even when the grinding apparatus is inclosed; and this demonstrates that the grinding operation is not entirely innocuous.

Our own observations and the data we have collected, allow us to state that the general manufacture of white lead is not so dangerous as some persons may believe, and this is proved by statistics collected in the hospitals of Paris for several years past. There are, however, great differences in regard to salubrity, between the different works we have visited. Nowhere have the old processes failed to receive some improvement; but, even the most perfect works are open to some objections in regard to the separation of the white lead from the non-corroded metal, and the dry grinding and sifting, which precedes the wet grinding between the horizontal stones.

Before proceeding further, we believe that it is now desirable to add a few theoretical considerations on the manufacture of white lead, which are due to Mr. Pelouze, who has paid great attention to that subject.

"The Holland process," says Mr. Pelouze, "which has been carried on at Lille, where it has become a prominent manufacture, consists in exposing sheet lead to the vapors of vinegar and to the gases of stable manure. The vinegar used is that made from inferior beer, and contains but a small proportion of acetic acid. From the examination I have made of that vinegar, and with the numbers furnished to me by MM. Lefèbre and Décoster, manufacturers of white lead at Lille, the weight of real acetic acid is less than 1½ per cent. of the weight of lead employed, and in good corroding operations nearly the whole of the metal is transformed into white lead. Mr. Graham, in England, has arrived at similar results, and with even a less percentage of acetic acid. It is therefore impossible that the carbonic acid of the white lead should be derived from the decomposition of the vinegar.

"Moreover, manufacturers are well acquainted with the fact, that no white lead is obtained when drafts are not established between the different parts of the beds.

"The theory of this process is therefore very simple. The air produces the oxidization, and the vinegar, volatilized by the heat of the fermenting manure, unites with the oxide of lead, being then displaced by the carbonic acid disengaged by the manure. A considerable portion of the acetic acid is found in the unwashed white lead made by the Holland process.

"I believe that such is the reaction, and since I have left Lille where I was able to study that manufacture, I have held this theory as being the most rational.

"I have made an experiment which well demonstrates the mode of action of the vinegar in the formation of white lead. I have compounded an artificial atmosphere of oxygen and carbonic acid, and in it I have placed a piece of sheet lead exposed to the vapors of vinegar in a cup underneath. After three months the lead was covered with a crust of white lead, the proportion of which was in the ratio of the oxygen and carbonic acid absorbed, whereas most of the vinegar was found in its previous state. The proportion of acetic acid causing the transformation into white lead was so small that it could not be ascertained.

"Another very curious experiment, in my own opinion, fully demonstrates the true action of acetic acid in the formation of white lead, and the necessity of employing in that manufacture an acid which may produce with oxide of lead a basic or subsalt which may be decomposed by carbonic acid.

"If in the preceding experiment we substitute for the vinegar formic acid which does not produce basic salts with oxide of lead, there is no white lead formed even after a contact of several years of the vapors of formic acid, the lead and the gases, oxygen and carbonic acid. Formic acid, however, is very near to acetic acid in its affinities and its volatility; but as it does not make basic salts with oxide of lead, and as the neutral formiate of lead is not decomposed by carbonic acid, it is therefore unsuitable for the manufacture of white lead."

Mr. Hochstetter thought, notwithstanding the preceding observations, that it was still necessary to directly ascertain whether air was the only oxidizing agent in the manufacture of white lead, especially in the Holland process.

Adding to his own experience the explanations of the above-mentioned chemists, he attributes the formation of white lead to two distinct causes in the Holland process:—

First, to the subacetate of lead which results from the contact of the air, lead, and acetic acid. This salt is decomposed into carbonate of lead and neutral acetate in an atmosphere saturated with carbonic acid and dampness.

Second, to the decomposition of the neutral acetate by wet carbonic acid. Carbonate of lead is produced and acetic acid is displaced.

For a long time it has been stated that white lead is not a neutral carbonate of lead, but a subcarbonate or a combination of neutral carbonate with a six basic acetate. The examination of this question was of practical interest, since the lesser consistency of the Holland white lead was due in the opinion of Mr. Mülder to the presence of an hydrated oxide of lead.

The author has therefore repeated the analyses of the latter chemist nearly in the same manner, and the results have been as follows:—

Krems' White.

		Washed.	Atoms.	Calculated.
Oxide of lead	83.77	83.97	8	84.06
Water	1.01	0.84	1	0.85
Carbonic acid	15.06	15.03	7	14.05
	99.84	99.84		

Precipitated White Lead of Magdeburg.

Oxide of lead	85.93	. . .	3	86.3
Water	2.01	. . .	1	2.3
Carbonic acid	11.89	. . .	2	11.3

White Lead of Unknown Manufacture.

Oxide of lead	86.40	. . .	3	86.3
Water	2.13	. . .	1	2.3
Carbonic acid	11.52	. . .	2	11.3

Krems' White.

		Washed.	Atoms.	Calculated.
Oxide of lead	86.25	. . .	3	86.3
Water	2.21	. . .	1	2.3
Carbonic acid	11.37	. . .	2	11.3

White Lead Prepared by the Author in Imitation of the Holland Process.

Oxide of lead	84.42	8	84.6
Water	1.36	1	0.8
Carbonic acid	14.45	7	14.5

These experiments prove, indeed, that none of the samples examined are a pure neutral carbonate, and that the missing carbonic acid is replaced by water. It seems, therefore, that white leads may often be variable combinations of carbonate and of hydrate of lead. We shall again examine this point further on.

The author has prepared a white lead by precipitating the subacetate of lead with carbonic acid until the liquor began to be acid. The precipitate perfectly washed with boiling water, gave:—

	Washed.	Atoms.	Calculated.
Oxide of lead	86.02	3	86.4
Water	2.44	1	2.3
Carbonic acid	11.45	2	11.3

Corresponding to the formula $2(PbO.CO^2) + PbO.HO$.

This white lead suspended in water and submitted for a long time to a stream of carbonic acid does not change. But if a few drops of acetic acid are added before the treatment with carbonic acid, it becomes neutral carbonate.

The author has prepared, by precipitation, numerous samples of white lead, and all had the composition of the French white lead. However, he does not decide on the question of the body or covering property, between the white lead prepared by the Holland and French processes. By microscopic examination no sensible difference of texture was detected, nor was any sample with a crystalline texture. If the good quality of white lead be due to the absence or to the presence of but a slight proportion of hydrate, it is now possible to obtain, by precipitation, a white lead answering to this condition.

3d. *The French or Clichy Process, by Thênard.*

Thénard was the first to point out a process for the manufacture of white lead, which was applied later by Mr. Roard in a large establishment near Paris, the products of which are known under the name of *Clichy white lead.* The chemical reactions on which this process is based are as follows:—

If a solution of basic acetate of lead, sometimes called *Extract of Saturn,* be treated with carbonic acid, part of the oxide of the salt is converted into carbonate of lead, and the remainder becomes neutral acetate. By adding a new proportion of litharge or oxide of lead to the solution of neutral acetate, this becomes basic again by the solution of the oxide. We see, therefore, that these reactions permit of the manufacture of white lead by a continuous and economical production of basic acetate.

Without thoroughly considering all the manipulations of this process we shall indicate the mode of operation.

A solution of basic acetate of lead, marking from 16° to 18° Bé., is made by boiling a solution of neutral acetate (sugar of lead) with very finely powdered oxide of lead (litharge). There is no difficulty in this operation.

When the litharge has become dissolved, and the basic solution is well saturated, the liquor is decanted from the impurities in the litharge or the acetate, into a closed vessel. Then the carbonic acid is introduced, which gas may be produced by several methods, such as the calcination of chalk or the combustion of carbon. At all events the gas should be previously well washed, so as not to add impurities to the white lead.

As soon as it is ascertained that all the basic excess of oxide of lead is transformed into carbonate, the liquors are allowed to settle. The carbonate falls to the bottom, and the supernatent solution of neutral acetate is decanted to be boiled again with oxide of lead, and become, as we have said, basic acetate.

There is, however, at each operation a certain loss of neutral acetate, which must be replaced and rendered as small as possible by careful manipulation.

The settled carbonate of lead is first washed with a small proportion of water, which is added to the decanted solution of acetate. The washing is then continued with larger quantities of water, which are thrown away, since they are too poor in acetate. The paste of white lead is put into pots, and dried in the stove room.

This Clichy white lead is in impalpable powder and as white as snow; but, compared with those of Krems and Holland, it has less density and body, that is, covers less.

The manufacture of white lead, by the Thénard process, has been established at Portillon, near Tours, by MM. Pallu and Delaunay, with a perfect understanding of its theory. Thanks to a report made in 1856 to the "Société d'Encouragement" by MM. A.

Chevalier, F. Barral, and Gaultier de Claubry, we are enabled to explain this manufacture.

Preparation of the oxide of lead.—The works of Portillon, as stated by the above delegates, contain five furnaces with double fire-places, four of which are in constant operation, and use bituminous coal as fuel. The furnaces are built directly in the rock, and calcine 1800 kilogrammes of lead at each operation. The leads employed bear the best brands of Andalusia and of England, and are analyzed at the works so that the best only may be received. The bed of each furnace is built with fire-brick holding as little silica as possible. The shape is nearly circular, about 3.40 metres in diameter, and with two lateral fire-places. It is hollow, so as to retain the molten metal. The vault is surbased, and 60 centimetres (0.60 metre) is the greatest distance between the bed and the ceiling of the vault.

During the heating, the gases of the combustion escape through an opening or hood, placed in front of the aperture used for charging the metal or extracting the oxide. This hood connects with an upper furnace where the transformation of the oxide of lead into red lead takes place.

Twelve hours are required for oxidizing 1500 kilogrammes of lead; but the oxide still contains a large proportion of metal or *blue lead*, which is separated and returns to the calcining furnaces. Half of the oxide produced is for the manufacture of white lead, and the other half for that of red lead.

Manufacture of the white lead.—The oxide of lead intended for the preparation of white lead is moistened with water, and spread over a wooden floor above two *saturating pans* lined with copper. These pans are supplied with stirrers composed of a wooden frame with bronze projections, which reach to about 1 or 2 centimetres from the bottom. One of the pans is raised above the other, so that the excess of liquid in the upper one may run by a spout into the lower one. The latter pan, at the middle of its height, is connected with a duplex bronze pump.

The two pans are filled with water rendered acid by about one-fortieth of pure pyroligneous acid marking 30 acetimetric degrees. While the stirrers are in motion, a certain proportion of damp oxide of lead is poured in, and becomes dissolved in part. The pump is then set to work, and forces the solution into three large tanks, lined with copper, placed in an upper story, and which connect with each other. These tanks have stirrers like those of the saturating pans, and which are kept in motion during the whole operation.

Besides the pipes for conducting the liquors, these three apparatus are provided with pipes and inverted gutters, perforated with numerous small holes, through which a continuous stream of carbonic acid escapes. The average specific gravity of the solution is 5° Bé.

During this operation the pump takes from the saturating pans the solution of basic acetate, and carries it into the precipitating tanks where it is brought into contact with the carbonic acid. The white lead is immediately formed, and the liquid, *which must still retain a certain proportion of basic acetate*, passes into the settling tanks where the white lead becomes deposited. The liquor then goes back to the saturating tanks, and the operation begins anew. It is, as we see, a system of circulation in which machinery performs most of the work, and hand labor is reduced to a minimum.

After a certain length of time, the settling tank is sufficiently filled with white lead, that is, when this material reaches the level of the overflow. The solution is then made to pass into other vessels and the white lead is washed in *washing tanks*, which are provided with wooden horizontal stirrers having a rotary motion.

The settled white lead is covered with twice its volume of pure water and stirred. Three washings take place, and at each, the material is allowed to deposit, and the water above is decanted.

The white lead is then conducted into large basins built of porous stones, which absorb part of its dampness. After a few days, the material is divided into blocks which are still quite wet, and which are pounded by wooden vertical stamps falling into a wooden trough inclined from the front backwards.

This stamping renders fluid the white lead which appeared half dry before. The stuff is then put into small movable boxes, holding about 400 kilogrammes, and which are carried to the drying-room. It is sufficient, for filling the pots, to open and close the trap-doors at the bottom of these boxes.

When the white lead is to be sold in powder, the stamped paste is run into wooden frames, which are set upon a brick platform heated underneath. When dry, it is put upon a distributor similar to that used for red lead, but larger, and which projects it upon a sheet-iron ventilator having four wings. The ventilator is inclosed within cast-iron plates, and is followed by a rectangular trough of the same metal, about 1 metre long. At the top end of the trough there is a sheet-iron pipe 35 centimetres in diameter, 8 metres long, and nearly vertical, which communicates at its upper end with a large sheet-iron chamber, to the bottom of which are fixed two funnels or hoppers closed by lateral sliding plates. Below the opening of the vertical pipe, and in the cast-iron trough, there is a cast-iron hexagonal prism which rotates and pulverizes the coarse portions of white lead which have not reached the upper chamber, and delivers them back to the ventilator. The white lead deposited in the iron chamber above is in impalpable powder.

The distributor, like that for red lead, has an aspirator, so that there is no danger of dust being inhaled by the men.

The above operations apply to the preparation of white lead in lumps and in powder, as is generally required by the trade. However, for several years past, part of the white lead has been ground in oil, which is a hygienic progress, since numerous cases of lead colic have been observed among those who grind white lead in the shops of color dealers.

The grinding of white lead in oil is done at the works of Portillon as follows: the stamped and still damp material is introduced into a kneading machine with the given proportion of oil, and soon transformed into dough, which is removed through a side opening. The paste is then ground between metallic rollers heated by steam, and the water expelled. After another passage through an ordinary grinding apparatus, the paste is put into zinc cans soldered or closed tight.

The carbonic acid used for the manufacture of white lead, and which passes through the solution of subacetate, is produced by the combustion of cheap charcoal dust, cemented into bricks by means of a small quantity of clay. The gas is aspirated from the combustion furnace by means of a series of inverted drums plunging into water, and which act as pumps.

Here are also a few data on a modification of this process, practised in England, and the description of which is due to Mr. Preisser.

The lead is smelted in a cast-iron kettle with a spout, which delivers it upon the bed of a large reverberatory furnace, in which air is constantly injected by a ventilator. The lead becomes divided, offers a large surface to the air, and runs into a channel the lateral sides of which are perforated with small holes. The lead is oxidized, and the litharge escapes through small apertures which may be opened at the same time. The silver, if any, remains at the bottom of the channel. This mode of preparing litharge is very easy and rapid.

The litharge is then finely divided, and, after being moistened with 1 per cent. of acetate of lead dissolved in water, is put into horizontal troughs, closed on top and communicating one with the other. A stream of impure carbonic acid, produced by the combustion of coke in a reverberatory furnace, with air projected by two powerful centrifugal ventilators, passes all the while through the layers of oxide. The pressure exerted by the ventilators is sufficient to overcome the resistance of the layers of litharge. The gases are cooled in pipes immersed in water.

In order to bring all the particles of oxide into contact with the carbonic acid, and aid the combination, a system of rakes, moved by machinery, keeps the mass constantly stirred.

The white lead obtained by this process is good for painting, and is perfectly white. It covers well, and is preferred in England to that prepared in the wet way, which contains crystalline particles.

4th. *Pattinson Process.*

By means of a chemical reaction, by double exchange of bases and acids, Mr. Pattinson obtains carbonate of lead on the one hand, and on the other a solution of lime salt, the nature of which depends on that of the lead salt employed. The salts which he perfers are the chloride and the nitrate.

Here are the chemical phenomena observed when carbonate of lime and chloride of lead react on each other. Equivalent proportions of these substances are triturated together, that is, 140 parts of chloride of lead, and 50 of carbonate of lime, and sufficient water is added to make a thin paste. After a certain length of time, indications of chemical reaction appear, the paste becoming thicker, drier, and nearly hard. Afterwards the solid mass begins to deliquesce, and soon resolves itself into a concentrated solution of chloride of calcium, and a white precipitate of carbonate of lead mixed with undecomposed carbonate of lime and chloride of lead.

After decanting the solution of chloride of calcium, and replacing it by pure water, the former decomposition continues; and if this operation be repeated several times, accompanied by trituration of the substances, the carbonate of lime and the chloride of lead are quite entirely decomposed, and the residue is nearly pure carbonate of lead. This complete decomposition requires from seven to fifteen days, and still there remain traces of chloride of lead and carbonate of lime, which may be detected by chemical analysis.

The reaction is quite similar, either in its nature or in the length of time required, when we triturate together equivalent proportions of nitrate of lead (166 parts) and of carbonate of lime (50 parts). Moreover, it has been ascertained that the decomposition of the nitrate or chloride of lead is more rapid when, instead of pure water, a solution of carbonic acid gas is employed. Indeed, carbonate of lime is soluble in water impregnated with carbonic acid, and is in a form which renders the reaction more rapid and complete. As soon as the soluble carbonate of lime has been decomposed the free carbonic acid causes the solution of another proportion, which is decomposed in its turn, and so on, the operation being continued with the same proportion of carbonic acid until the decomposition is complete, if the mixture has been made in accurate chemical proportions.

But as the water impregnated with the carbonic acid becomes by degrees a more and more concentrated solution of lime salt, it is preferable, towards the end of the operation, to replace it by fresh water holding carbonic acid. It is even better to change the water several times, so as to insure the decomposition of the entire carbonate of lime employed. It is also necessary to stir the contents frequently.

After these observation we now pass to the practical process of the white lead manufacture.

The mill in use is similar to that employed in pottery and earthenware factories for grinding flint stones in water. A strong wooden tank, bound with iron, has its bottom filled with blocks of quartz or of French burr, cemented together, and with a level surface. Other large stone blocks are made to revolve over the lower surface, and grind to a fine powder the hard and brittle substances which have been put into the mill with the addition of water. For our purpose the running stones need not be so heavy as in pottery works, because the materials do not require the same degree of comminution. We should avoid employing iron whenever this metal may be in contact with the ground substances, and use copper for the metallic parts of the inside of the tank.

In a mill of that kind, 4 metres in diameter and 1 metre high, the charge is 1066 kilogrammes of chloride of lead and 380 kilogrammes of carbonate of lime, the best of which is washed chalk. As much water is added as will just not run over by the motion of the stones, and the grinding operation lasts six hours. After that the tank is almost entirely filled with water, and allowed to stand till the next day, when the deposit is found to be carbonate of lead mixed with the undecomposed carbonate of lime and chloride of lead. The supernatant liquor is a clear and concentrated solution of chloride of calcium, nearly free from lead, and which is decanted by means of a siphon or a stopcock. A new quantity of water is put into the mill, and the grinding is repeated for a few hours, followed by a settling and a decanting on the next day, and so on, until from the seventh to the fifteenth day, when the solution has no taste, and the decomposition is complete.

The white substance at the bottom of the mill is nearly pure carbonate of lead, with but traces of chloride of lead and carbonate of lime, and is removed, dried, and prepared in the ordinary manner for the trade.

A modification of this process consists in adding, at first, an excess of chloride of lead, that is, 1264 kilogrammes for 380 kilogrammes of carbonate of lime, and grinding, settling, and decanting the liquors until all the carbonate of lime is decomposed, which is ascertained by the absence of a bitter taste in the solution. Then the excess of chloride of lead is transformed into carbonate by the addition of about 200 kilogrammes of soda crystals, or an equivalent proportion of carbonate of potassa. The liquor should remain slightly alkaline. The grinding is continued until all the chloride of lead has become carbonate; and, afterwards, the chloride of sodium or potassium is removed by washing. In this manner the length of the operation is shortened and the carbonate of lead is purer.

The inconvenience of this method is that, beside the greater expense due to the alkaline carbonate, a small proportion of chloride of lead is dissolved in the washing liquors before the carbonate of lime is throughly decomposed. It is true that the lead may be recovered from the last washings by a precipitation with a sulphide of potassium or sodium.

If, instead of grinding in pure water, we use a solution of carbonic acid, the operation is performed as follows: A vessel, barrel-shape, which may be of wood, copper, or lead, and about 0.75 metre in diameter and 1.20 in height, is tightly bound with iron, and has its heads sufficiently stout to resist the necessary pressure. It revolves upon two trunnions, one of which carries a fast and a loose pulley, so that motion may be given or arrested at will. The other trunnion is hollow, and has a stopcock communicating by a universal joint with the pump, which forces the carbonic acid into the vessel.

Through a side opening, 50 to 75 millimetres in diameter, 70 kilogrammes of chloride of lead and 25 kilogrammes of carbonate of lead are introduced. The vessel is then nearly filled with pure water, the opening is closed with a screwed plate, and carbonic acid is forced through the hollow trunnion under a pressure of from four to five atmospheres. After closing the stopcock, the barrel is set in motion, and revolves about twenty times per minute. The substances begin to react one upon the other: the carbonic acid with which the water is saturated dissolves the carbonate of lime and presents it to the chloride of lead in such a state that the decomposition is immediate. The reaction is continued for two or three days, and is then so near the end that but little carbonate of lime and chloride of lead remain undecomposed; and, in their stead, there is carbonate of lead and a concentrated solution of chloride of calcium. The motion of the barrel is then discontinued, and, when the contents have had time to settle, the clear liquid is siphoned off through the lateral opening and replaced by fresh liquor, which is saturated with carbonic acid as previously. The barrel is made to revolve for two or three days more, when the decomposition is completed, and the carbonate of lead obtained requires but a thorough washing and drying.

In this second mode of operation an excess of chloride of lead may be employed to promote a more rapid decomposition of the carbonate of lime. The remaining chloride of lead is decomposed in the barrel with a slight excess of an alkaline carbonate, as we have already explained.

When nitrate of lead is employed the operation is the same as with the chloride, whether we use pure water or that saturated with carbonic acid. The equivalent proportions are for the stone mill—1264 kilogrammes of nitrate of lead and 380 kilogrammes of carbonate of lime, and, for the revolving vessel, 83 kilogrammes of nitrate of lead and 25 kilogrammes of carbonate of lime.

In either case the substances are allowed to react upon each other until the decomposition is complete. The resulting white lead is then washed, dried, and packed in the usual manner.

Sometimes, also, a solution of carbonate of lime in water saturated with carbonic acid is effected in the revolving apparatus, and is poured into tanks holding the solution of either chloride or nitrate of lead. A pure carbonate of lead is immediately precipitated.

We shall now quote from Mr. F. Heeren, a manufacturing chemist, who has carefully studied a peculiar white lead, prepared by another Pattinson process.

"The white lead of Mr. Pattinson is distinguished from the ordinary kind by its composition, which is a basic chloride and an oxychloride of lead, instead of a combination of oxide of lead with carbonic acid.

"Mr. Pattinson prepares his white lead from crude galena (sulphide of lead) abundant in England, and which often contains silver. This latter metal is entirely collected, and the sulphur is also employed.

"The finely powdered galena is heated in closed lead vessels with concentrated hydrochloric acid, which is produced in large quantities in soda works, and which is very cheap. By this treatment the sulphur is transformed into hydrosulphuric acid (sulphuretted hydrogen) which is burned in the furnace of sulphuric acid chambers, and thus assists in the production of sulphuric acid. The lead is transformed into chloride, and as this salt is but slightly soluble, large volumes of boiling water are employed in order to separate the sulphide of silver contained in the gelena. The boiling solution of chloride of lead, in order to pass to the basic state, needs to be mixed with lime-water. It is absolutely necessary that the mixing should be effected very rapidly in order to obtain the basic chloride of lead in the shape of an exceedingly fine powder which covers well. A slow and gradual mixing results in a crystalline precipitate which does not cover well.

"Another condition is that the proportion of lime should be exactly calculated for neutralizing half of the chlorine of the chloride of lead, and that the precipitated basic salt should contain equal atoms of chloride and of oxide of lead. The clear solution of lime is in one tank, the hot one of chloride of lead is in another tank, and they are mixed together by regulating their running into a third tank by means of stopcocks.

"One inconvenience of this manufacture is, that, the chloride of lead being but slightly soluble even in boiling water, very large vessels are needed, and the consumption of fuel to heat the water is considerable. A neutral chloride of lead requires about twenty-two times its own weight of boiling water to be dissolved, and theoretically for fifty kilogrammes of Pattinson's white lead 1219 litres of boiling water are required for the chloride of lead, plus 4420 litres for the lime, altogether 5639 litres, occupying a cube having 1.80 metres in every direction.

"When experimenting with this process on a small scale, I have found out another difficulty, *i. e.*, when powdered galena is treated with hydrochloric acid, the surface of the grains is soon coated with chloride of lead which arrests the action of the acid. The entire galena is dissolved only when a large excess of hydrochloric acid is employed sufficient to dissolve the whole of the chloride of lead formed. However, the expense of such an excess of acid may be avoided by decanting the hot solution into another vessel as soon as the action ceases, and allowing it to become cold and to deposit the chloride of lead. The cold acid is decanted and used again upon the galena, and when saturated with chloride let to cool off.

"The chloride of lead thus obtained and drained, is washed with small proportions of cold water in order to remove the free acid and any iron salt which otherwise would discolor the white lead. It is then dissolved in boiling water.

"Several samples of Pattinson's white lead which I have examined, are not pure white, but with a slight brownish shade which is scarcely sensible when a small proportion of black or blue is added to them. On the other hand, it covers particularly well. I have ground equal parts of Pattinson's and Krems white lead with equal proportions of oil, and I painted with them surfaces of equal area; the Pattinson white lead had evidently the best covering power. It is very bulky, possesses great body, and absorbs a large proportion of oil."

5th. *Woolrich Process.*

Commercial lead is granulated by means similar to those used for making lead shot, and the granules are put into a cylindrical or hexagonal stoneware vessel, which may be made to revolve upon a central shaft passing through two holes at the opposite ends of the vessel. During the motion the lead is kept constantly wet with a neutral solution of acetate of lead of specific gravity 1.6. By the mutual attrition of the granules of lead, aided by the above solution, particles become separated which are washed out every twelve hours. Fresh proportions of granulated lead moistened as we have said, are then added to make up the loss by attrition and decomposition. The separate particles with the washings are collected in a closed vat, through which is injected carbonic acid produced by the combustion of charcoal or coke. The substances are kept stirred by proper machinery, and there is produced a carbonate of lead which settles in a few hours, and is removed after the washing liquors have been decanted.

A hexagonal vessel 55 centimetres in diameter, and 1.60 metre high, will hold from 400 to 500 kilogrammes of lead.

6th. *Versepuy Process.*

An Italian once made the observation that when granulated lead is comminuted by friction, it becomes transformed into white lead by absorbing carbonic acid. Mr. Versepuy thus states the improvements he has brought to that system:—

"Fragments of lead are put into a stone cylinder (made of Volvic lava if possible) and covered with water. After twelve hours of rotary motion, the metallic mud is poured into a wooden tub having a wooden stirrer in the middle and two ventilators on the upper surface with the proper capping to prevent the liquor from running over.

"The inside surfaces of the stone cylinder become coated with a layer of white lead which prevents further waste of stone, and is believed to act as a leaven for the oxidization of the molecules of lead during the further operations.

"It is not necessary in a regular operation to employ lead in a thorough state of division.

"Water is necessary for separating the particles of lead produced by mutual attrition.

"The metallic mud should be removed from the stone cylinder and from the undivided lead, in order to aid its oxidization by an energetic stirring.

"The carbonic acid of the air is sufficient to produce the carbonate, and no advantage has been found in the use of artificial carbonic acid or of an atmosphere of this gas in the tub. The same may be said of an addition of acetic or nitric acid or of one of their salts.

"This process, as we see, is very easy and economical. The operation is not complicated by the addition of any chemical agent, and mechanical manipulation alone is sufficient to bring about the transformation of the metal into white lead.

"In this process everything favors the manufacturers of lead who own the raw material and may utilize the water-power generally abundant in the neighborhood of mines."

Since giving this description, Mr. Versepuy has improved his processes, which are thus described in his patent of July 15th, 1846:—

"I propose to oxidize lead at the ordinary temperature, under the influence of an energetic stirring, and of the intimate and simultaneous contact of the metal with air and water. The oxide thus obtained is carbonated by a liquid constantly saturated with carbonic acid.

"The process may be divided into three distinct operations:—

"First, the division of the lead to as great an extent as practicable, in order to obtain large surfaces of corrosion.

"Second, the oxidization of the lead by the oxygen of the air, and the immediate removal of the pellicle of oxide by washing and stirring. The oxidization may be aided by an energetic oxidizing agent, an acid for instance.

"Third, the carbonatation of the oxide by its contact with carbonic acid gas obtained by any desired method.

"I know that similar processes have already been tried, but the experimenters have never succeeded, because they were not sufficiently aware of the importance of each operation and of its results. They have never employed a current of air sufficiently energetic to furnish enough oxygen to the metal—or an auxiliary oxidizing agent—or a subsequent, distinct, and well-conducted carbonatation.

"Here is the mode of operation which I found to succeed best:—

"I. The lead is melted in a closed furnace, which is a protection against the fumes being inhaled by the men, and poured into cold water through a fine metallic sieve. Small and light granules are thus obtained which present a great surface to corrosion.

"II. The granulated lead is placed in the cylinder F (Fig. 1), with one-fifth of its weight of water, and a small proportion of some oxidizing agent. A pipe K brings into the cylinder a brisk current of air, forced in by means of a fan or of a screw-blowing machine like Fig. 2. The pipe K passes through the stuffing-box I, and the air is divided by a rose at J, before it escapes from the cylinder at J′. A rapid rotary motion is imparted to the cylinder, the inside metal parts of which are of lead, in order not to injure the oxide. The friction of the granules together and against the sides of the cylinder, at the same time with the chemical reaction which takes place, gives an increase of temperature of from 55° to 60° C., and it is important to keep it up by making the operation continuous. The rotary motion of the cylinder should not be too rapid, so as not to keep together by centrifugal force the mass of granules, which, on the contrary, should fall and describe a curve. This operation lasts about twenty-four hours, and then the thick and yellowish liquid is removed from the cylinder.

Fig. 1.

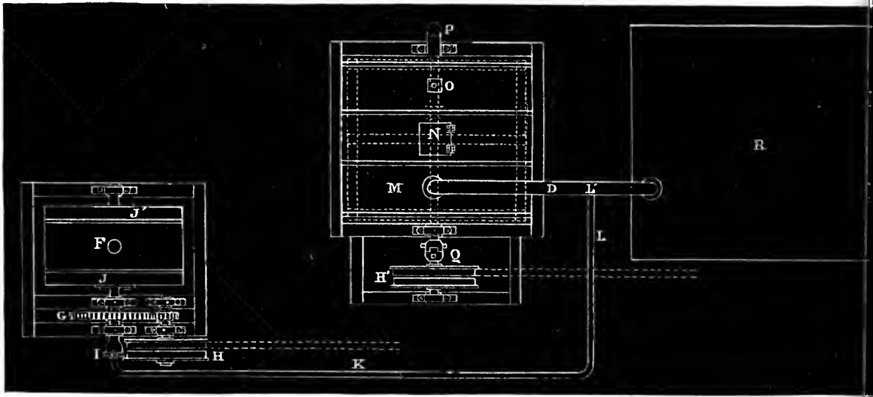
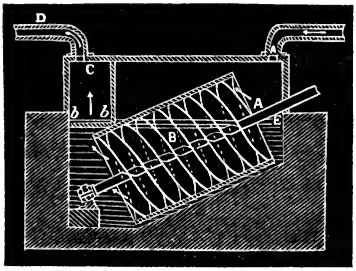


Fig. 2.



"III. The above mixture is diluted with twice its weight of water, and poured into the cylinder M, which may be of wood lined with lead. An inner stirrer presents fresh surfaces to the action of carbonic acid, and makes at least one hundred and fifty evolutions per minute. A pipe D brings in the carbonic acid gas produced by any desired method, and forced in by mechanical action.

"It is possible to use the small proportion of carbonic acid held in atmospheric air, in which case the carbonatation is slow, or the carbonic acid gas emanating from mineral springs, or from the reaction of an acid upon a carbonate, or that produced in a lime-kiln or from a fireplace. In the latter cases, a screw-blowing machine, Fig. 2, is very suitable, since the gases are cooled and separated from the ashes in the water of the apparatus.

"In from fifteen to thirty minutes, according to the quantity of material in operation, the action is complete, the mass of oxide becomes white, and there is an elevation of temperature of from 60 to 65° C. The white lead and water may then be removed.

"It is well understood that the stream of carbonic acid escaping from this cylinder passes into other similar apparatus to complete its condensation.

"The white lead thus produced is by the usual processes brought into the commercial shape."

In an addition to his patent (July 15th, 1847), Mr. Versepuy expresses his disbelief in the usefulness of an auxiliary oxidizing agent.

7th. *Wood, Benson, and H. Grüneberg Processes.*

We owe to Mr. Wood a process for manufacturing white lead, which consists in introducing granulated lead and water into a revolving and horizontal hexagonal box, the two ends of which have openings for the circulation of the air. A hydrated protoxide of lead is formed, which is removed through a side opening provided with a sieve, and which is saturated separately with carbonic acid.

Mr. Grüneberg, after a careful study of this method, found out that a cause of failure was the formation, in the revolving apparatus, of a peroxide of lead conjointly with the desired protoxide. By the treatment with carbonic acid, the peroxide remains as such, and colors the white lead a pink or reddish hue. As proof that this coloration is due to the peroxide, the white lead is dissolved in diluted nitric acid, and if the washed residue be treated with hydrochloric acid and a gold leaf, the latter becomes dissolved, thus showing the presence of a peroxide.

Nevertheless, Mr. Grüneberg uses for his process the Wood apparatus, that is to say, a hexagonal revolving prism made of stoneware unacted upon by acids. During the operation, the lead is submitted to the simultaneous action of atmospheric air, acetic acid, and carbonic acid gas. The atmospheric air enters through openings on the heads of the prism, and the acetic and carbonic acids through the hollow axis.

In order to aid oxidation, the inside of the apparatus is provided with projecting ribs, which cause the lead to fall down and to present fresh surfaces to the action of the air. By means of the simultaneous reaction of the air, of the solution of acetate of lead, and of carbonic acid, the process resembles the Holland method, except that it takes place in a revolving apparatus. The conditions are excellent, since the film of white lead on the surface of the metal is constantly removed and fresh metallic surfaces are presented to the chemical agents. Eight days are sufficient by this method for completely transforming into white lead a given weight of lead which would require two months by the Holland process.

The mutual friction of the lead, and the chemical reactions which take place, cause an elevation of temperature which is very advantageous and prevent any crystallization of the white lead. This pigment, washed out now and then from the apparatus, is so fine that the ordinary operations of grinding and floating are entirely unnecessary.

The mechanical motion added to the chemical reactions, gives in one operation a product which simply needs washing and drying to be ready for sale. The formation of a peroxide is also avoided, since, as soon as the protoxide is formed it changes to a basic acetate, and has no time to absorb a larger proportion of oxygen.

However simple this process may appear, it nevertheless presents many practical difficulties, and the oxidation requires a great deal of care.

The introduction of air and carbonic acid should be effected in certain fixed proportions. An excess of carbonic acid does not produce the neutral carbonate of lead ($PbO.CO^2$) and the liquid in the apparatus is all in a foam which envelops the lead and prevents the access of the air. Thus, no oxidation takes place, and the yield of white lead becomes low.

We should endeavor to produce the compound $2(PbO.CO^2) + PbO.HO$, and, on that account, the substances inside of the revolving apparatus should be kept in the basic state. This condition is ascertained by trying the liquors with yellow turmeric paper, which should turn brown. A basic milk of white lead does not foam, but runs smooth and leaves the granules of lead perfectly clean and ready to be oxidized.

There should never be so much carbonic acid as completely to decompose the basic acetate of lead, but merely the proportion necessary to saturate a quantity corresponding to the oxide formed. But as it is not easy to remain always within the proper limits, it will be well frequently to test the liquors with the turmeric paper.

The basic excess of hydrated oxide of lead should not, however, remain with the white lead, because it renders the oil paints made with this pigment yellow. Indeed, this oxide PbO.HO forms with the fatty acids of the oil, a colored soap which requires a long time to become decomposed by the action of light and the carbonic acid of the air. By its transformation into carbonate of lead, the desired whiteness reappears.

Moreover, a white lead with an excess of PbO.HO has a great specific gravity, and as demonstrated by analysis, has a composition near to the formula $3(PbO.CO^2) + 2(PbO.HO)$. This excess of oxide is removed by adding to the thin paste of white lead, enough acetic acid to prevent the turmeric paper from becoming brown. The white lead has then the composition $2(PbO.CO^2) + PbO.HO$ which is a durable combination without basic properties.

As this operation cannot be well done in the revolving apparatus itself, the white lead is washed off with a very weak solution of subacetate of lead, into a special tub where it is treated with acetic or carbonic acid. The neutralized white lead is then allowed to settle at the bottom of other tubs, and the solution of subacetate is employed again for the oxidizing operation. The deposit is finally washed with pure water and drained in a centrifugal apparatus.

The ordinary centrifugal apparatus with perforated sides cannot be used for this purpose, because the paste of the white lead soon clogs up the cloth spread inside of the drum, and the water cannot be forced out. It has therefore been thought more advantageous to separate the water from the white lead by means of the difference in their specific gravities, according to the law that the centrifugal power of a body is proportional to its increase of specific gravity. After having tried a revolving drum without holes on its sides, it was found that the thin paste of the white lead was not following the same rapid motion of the drum, and that by bringing the apparatus to a rest, the water was diluting the white lead again. In order to obviate this inconvenience, radial partitions were put inside of the drum, and these carrying the liquid with them, a complete separation took place in ten minutes. The white lead, as a thick paste, lies against the sides of the drum, and the clear water is on the top of it and may easily be decanted. The white lead is then put into pots, and dried first at the ordinary temperature, and afterwards in a stove.

The white lead prepared by this process remains wet until it is packed, and there is no danger of its dust being inhaled by the workmen. Nearly all the work is done by machinery.

Observed under the microscope, this white lead shows no angular or translucent parts; it is formed of exceedingly small spheres, scarcely as large as those obtained by the Holland process. These spheres are entirely opaque, and this quality, with their fineness, explains their great body or covering power.

The composition of this white lead, in the various stages of its manufacture, is determined by decomposing a sample of it, dried at 120° C. with nitric acid in the Geisler apparatus for determining by loss the carbonic acid. Another portion of the dried substance is melted in a covered porcelain crucible, so as to ascertain by loss the carbonic acid and water. After deducting the carbonic acid of the first test, the difference or water allows of the calculation of the hydrated protoxide of lead. On the other hand, the proportion of carbonate of lead is calculated from that of carbonic acid.

An analysis of the white lead manufactured by this process gave :—

PbO	86.34
CO^2	11.34
HO	2.32
	100.00

And, as the calculated composition of the formula $2(PbO.CO^2) + PbO.HO$, is

PbO	86.37
CO^2	11.32
HO	2.31

we see that the manufactured product contains a slight excess (0.12 per cent.) of neutral carbonate of lead.

In the Benson process, modified by Mr. Wollner, finely pulverized litharge is introduced into a long horizontal wooden cylinder, with about 1 per cent. of neutral acetate of lead, and sufficient water to make a thin paste. The apparatus revolves slowly, and a continuous stream of carbonic acid gas, obtained by the combustion of coke; is introduced through the hollow axis. In order to absorb this gas as thoroughly as possible, it is made to pass through several similar cylinders connected together. The evaporated water is replaced and the paste kept in a semi-fluid state. After a few days all the litharge is transformed into white lead, which is ground in two consecutive mills, and compressed and dried.

Mr. Grüneberg has still modified this process by adding to the litharge about 50 per cent. in weight of granulated lead. The latter not only reduces to a great degree of comminution the white lead formed, but also causes by its oxidation an elevation of temperature which aids the operation considerably, since the litharge is transformed into white lead in half the time previously necessary. This white lead does not require any further grinding, being already finer than the ordinary ground white lead, and having great body.

It has often been observed that in this process or that of Mr. Benson, the ordinary commercial litharge is not sufficiently pure, being often contaminated with the oxides of copper and iron. The oxide of copper imparts to the white lead mixed with oil, the property of soon becoming yellow in contact with the air; and this is explained from the reduction of the copper oxide by the essence of turpentine mixed with the paint. For instance, a sample of white lead, strongly impregnated with oxide of copper, was ground with linseed oil and turpentine, and spread upon a pane of glass which was then exposed to the air and the light. After a few days the coat had become yellow, and, being scraped, was treated with ether in order to dissolve the oil. The residue was then dissolved in hydrochloric acid, filtered rapidly, and the filtrate treated with ammonia. The liquor was colorless at the beginning, but became blue by degrees from the top. This proves the presence of the oxide of copper. Another sample of the same white lead was also ground with pure linseed oil, without turpentine, and spread upon a pane of glass. After exposure to the light and the air the coat remained white, which proves that the yellow discoloration was due to the essence of turpentine.

A fine commercial white lead requires, therefore, that the litharge be free from copper. The finely powdered oxide of lead may be treated with a solution of carbonate of ammonia until the liquors are no longer colored blue. But, as this operation is slow and somewhat costly, it is preferable to transform into litharge a pure metallic lead, and the white lead will not then become yellow.

We may add a few observations on the chemical states in which oxide of copper impairs the colors of white lead paints, or, on the other hand, does not injure them sensibly. It has been observed that, when the liquors holding copper were precipitated by carbonate of soda, the paint remained perfectly white. This fact is easily explained theoretically, since the carbonate of copper is not, like the oxide, reduced by the essence of turpentine. As a proof, the following experiments were made:—

I. 500 grammes of Goslaer litharge were transformed into white lead by the Benson process, with a solution of neutral acetate of lead and a stream of carbonic acid. The product was well washed and dried.

II. An equal quantity of the same litharge was very finely powdered, and treated with a solution of carbonate of ammonia until fresh liquors were no longer colored blue. This litharge was then transformed into white lead, like the former sample.

III. 500 grammes of the same litharge were dissolved, without previous purification, in the shape of a solution of subacetate of lead, which, after fitration, was completely precipitated by carbonate of soda. The product was well washed and dried.

The white leads obtained by these three methods were ground in linseed oil and essence of turpentine, and coats laid over equal surfaces.

No. I. began to turn yellow after twenty-four hours. No. II. remained perfectly white. No. III., which had as much copper as No. I., but in the carbonate state, was not discolored.

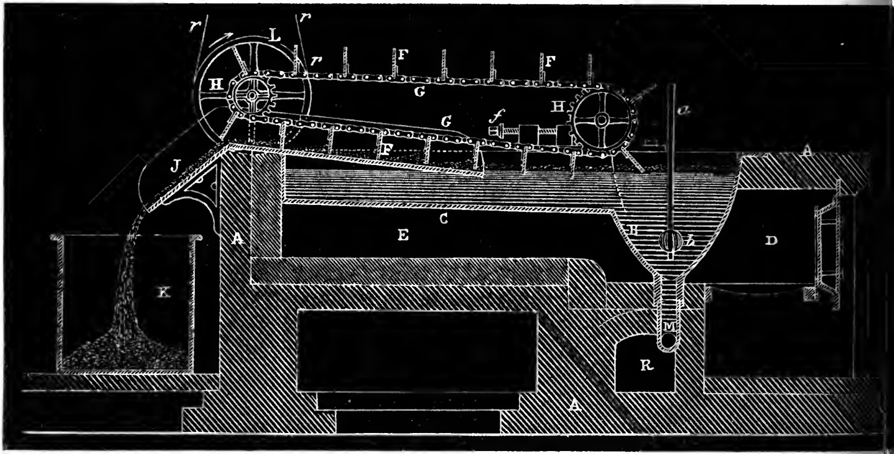
It results from these experiments that, in general, copper in white lead may be the cause of its turning yellow, when the metal exists in the form of oxide (CuO), but not in that of carbonate.

8th. *Mullin's Process.*

The improvements claimed in the patent of Mr. Mullin are: *First*, A process for the separation of metallic oxides from the fused metals, by forcing gases or atmospheric air through the metallic mass by means of a compressing apparatus. There are also the means of removing the alloys, or the oxides from the surface of the bath. *Second*, A process for the manufacture of white lead by submitting the oxides to the fumes of vinegar and to carbonic acid. *Third*, The employment of magnets for separating the iron from the metals with which it is mixed.

I. The apparatus for melting the metals and separating the oxides (Fig. 3) is composed of a furnace A A, supporting a kettle or boiler B C, which is heated by the fireplace D. A tube *a* terminated by a ball *b*, hollow and with longitudinal slits, is immersed in B, and communicates in an upper story with a holder *c* (Fig. 4), in which a pump *d* compresses the gas or air, or their mixture, which passes through the fused metal and oxidizes it. The flow of gas or air is regulated by the valve *e*.

Fig. 3.



The oxide is removed by the revolving rake F, the endless chain of which is carried by two pulleys H H. The tension is regulated by the screws *f f*, and the oxide passes upon the inclined spout J, which is made of iron rods sufficiently close to retain the oxide, and hot enough to melt the non-oxidized metal, and return it to the bath. The oxide falls into the box K.

The tube *a* may raised or lowered by means of the counterweight *h* and the flexible tube *g*. Two safety valves *i j* are placed, the one upon the pipe *k*, and the other upon the holder *c*. To the latter is also added a gauge *l* to indicate the pressure, which should be sufficiently energetic to overcome the column of molten metal, and to maintain a constant flow of gas. Another pipe *m* connects the pump *d* with a gas holder, when gas, instead of atmospheric air, is employed. In the case of air, the pipe *m* is disconnected at *n*. The piston of the pump *d* is set in motion by the side rod *o*, attached to the crank *p* which is fixed on the same axis as the pulley *q*.

Fig. 4.

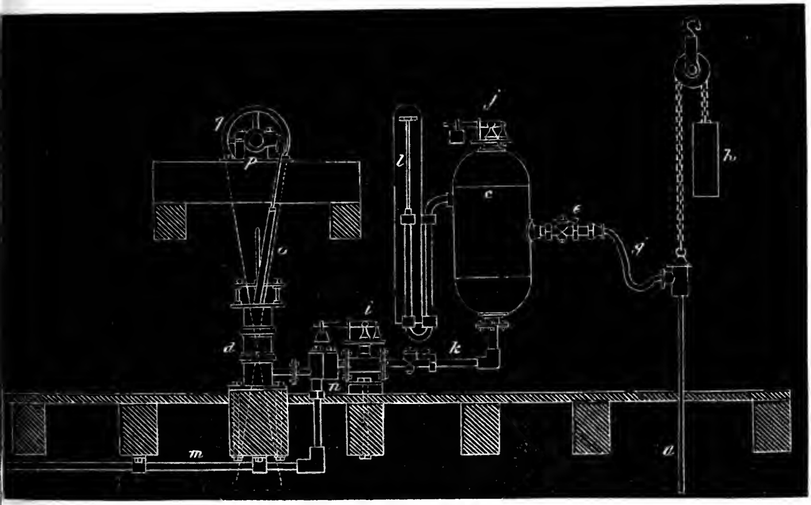


Fig. 5 shows the disposition which prevents the admixture of the metal with the oxide. The inclined metallic plate A, of iron or other metal, is attached to the pipe B, a little above the perforated ball C. The current of air is conducted by A up to the edge F of the kettle, and there is no agitation on the surface of the bath, where the oxidation takes place.

Fig. 6 explains another mode of oxidizing metals. Black oxide of manganese is put into the iron pot A, having holes at B and D, and a handle S. When this pot is immersed in the bath, the metal penetrates through B, and heats the manganese, which disengages oxygen and rapidly oxidizes the metal.

Fig. 5.

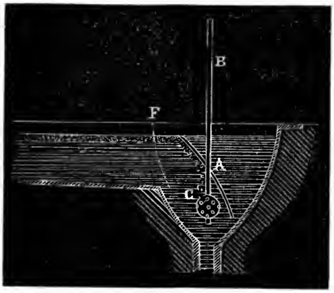
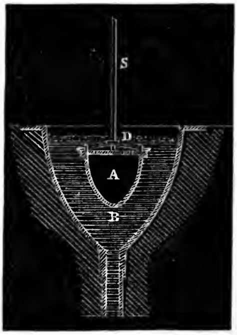
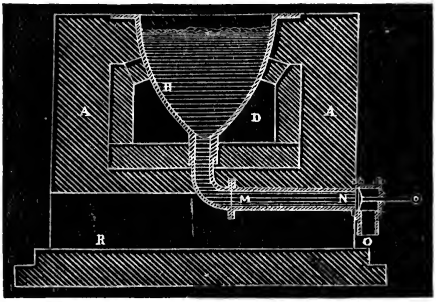


Fig. 6.



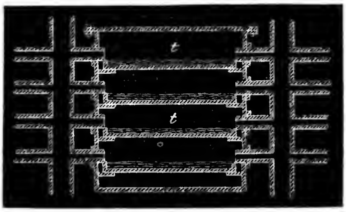
If the metal employed be lead holding silver, the latter, not being oxidized, goes down to the bottom of the kettle, from which it is removed through the plug N (Fig. 7), of the pipe M O, which is kept hot by a fire at R.

Fig. 7.



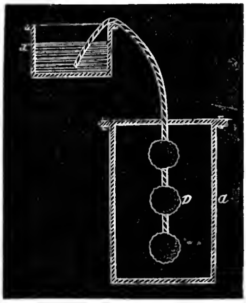
II. The oxide of lead obtained by any one of these processes is ground, sifted, and washed, and then put into the trays *t t* (Fig. 8), which are lined with lead and hermetically closed with covers. These trays are placed in a lead box, and the room is kept at a temperature of from 38° to 48° C. The layers of oxide of lead are about 3 centimetres thick, and are kept wet with water. When the apparatus is filled with the litharge, then begins the introduction of the fumes of vinegar distilled in an ordinary still, and of carbonic acid kept in a gas holder in an adjoining room. Before removing the covers of the trays, the stopcocks in the pipes through which the vinegar vapors and the carbonic acid pass are turned off. By these means, when the proper temperature has been maintained, the oxide of lead is transformed into carbonate.

Fig. 8.



Another method of manufacturing white lead, proposed by the same inventor, consists of a series of large stoneware jars *a* (Fig. 9), in which are suspended, by woollen or cotton cords, several sponges *v*, which do not touch the sides of the jars. By capillary attraction, a solution of neutral acetate of lead held in *x* keeps the sponges wet. The salts of lead are transformed into carbonates by a current of carbonic acid which passes through the jars. The sponges are then removed, and washed in pure water. After settling, the clear liquors are decanted for a future operation.

Fig. 9.



III. Should the metallic oxides contain iron, this is removed in the following manner: A wooden table or trough *y* (Figs. 10 and 11) is furnished with a certain number of magnets *z*, the poles of which pass

Fig. 10.

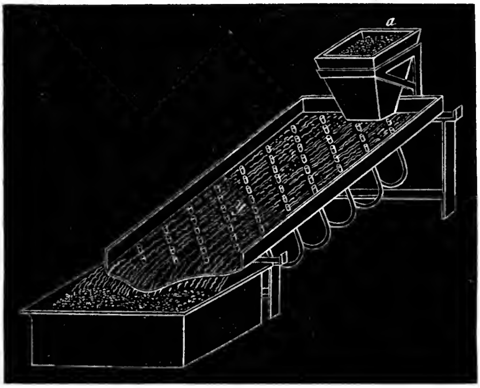
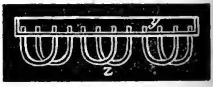


Fig. 11.



through the bottom of the table. The latter is inclined 30° and has a slow oscillating motion. The oxide is delivered by the hopper *a*, and the iron is arrested by the magnets.

9th. *Schuzenbach Process.*

Carbonate of lead may be produced by a great many chemical decompositions, but the product is not white lead. Nevertheless the inventors are not to be discouraged, and have tried many ways of arriving at results more or less satisfactory. There are a great many processes described, some of which show great ingenuity. On that account, and in order to give some idea of what has been done in that direction, we shall examine several of these methods.

The principal inconvenience of the ordinary processes for the manufacture of white lead, is that they are unhealthy. The method proposed by Mr. S.

Schuzenbach, of Friburg, seems to be entirely wholesome. It is also said to require less capital, and less room, and to give a larger product.

In a room so arranged as to be heated from 40° to 60° C., several wooden tubs are placed close to each other. These tubs are filled with alternate layers of shavings impregnated with vinegar, and lead plates or buckles, each layer being separated by perforated wooden partitions which can be easily removed, and allow of the free circulation of gases and vapors. The tubs are then closed with wooden covers, and kept at the proper temperature until the shavings have become dry. The lead buckles, which are almost entirely corroded, are then removed and deprived of the adhering white lead by being placed in water. The shavings being moistened with vinegar, the operation may be begun anew.

The white lead thus produced should always be washed with pure water in order that the various acetates of lead, copper, or iron, be dissolved and separated from the insoluble carbonate. After several washings, the product is dried.

The first waters employed for washing, may be decanted for saving the acetates of lead or copper still held in them.

10th. *Sewell Process.*

This process comprises four distinct operations: *First*, an improved method of making oxide of lead; *Second*, the production of a white lead of superior quality, which contains less carbonic acid than the average commercial white lead; *Third*, the employment of carbonic acid produced by other means than by combustion in the air; *Fourth*, a mode of washing the white lead, by which the foreign substances are removed.

I. The incompletely oxidized lead, that is, that mixed with a certain proportion of metallic lead and red lead, is kept at a red heat in a reverberatory furnace for three or four hours, and stirred all the time. When the whole has become transformed into protoxide of lead, it is immediately thrown into a closed vessel to prevent further oxidization by contact with the air.

II. During the second operation, the solution of oxide of lead is precipitated either by an alkali combined with a certain proportion of carbonic acid, or by carbonic acid alone. In the first case, the oxide of lead is dissolved in weak nitric or acetic acid, and to the solution is added potassa, soda, or ammonia, in quantity sufficient to neutralize the acid. When carbonic acid is used, the solution of acetate of lead is stirred all the time that the gas is passing through it. As soon as the solution acquires an acid reaction the flow of carbonic acid is stopped.

III. The carbonic acid may be obtained by mixing one part of coke dust with seven parts of finely pulverized sulphate of lime, or ten of sulphate of baryta, or eight parts of sulphate of strontia. These various mixtures are kept at a cherry-red heat in an ordinary gas retort as long as carbonic acid is produced, which, after cooling over the water of the main pipe, goes to a gas holder before being used in the manufacture of white lead.

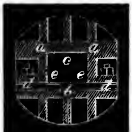
Another method of generating carbonic acid gas consists in passing steam through a clay retort filled with finely broken coke and kept at a cherry-red heat. The steam is decomposed, and carbonic acid and other gases are produced and collected in a gas holder.

IV. The white lead is washed under pneumatic and hydrostatic pressure, in order to remove the acid and other substances before it is dried.

Explanation of the Apparatus.—Fig. 12 is a transverse section of a cast-iron receiver *a a* lined with copper, in order to prevent the contact of the white lead with the iron. *b*, cover held by screws. *c*, space occupied by the white lead which is to be washed.

Fig. 13 is a section of the inverted receiver with its cover on.

Fig. 13.



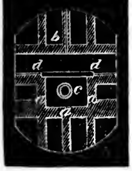


Fig. 12.

Fig. 14.

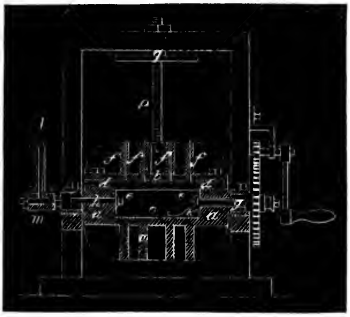


Fig. 14 is a longitudinal section of the same receiver, held in a wooden frame.

Fig. 15 is another longitudinal section, but in an inverted position, which is that of the apparatus during the operation. The groove at *d d* is packed tight with tow when the cover is on. A thick brass plate *e e* (Figs. 16 and 17), perforated with holes, is attached to the cover. The holes are slanting near the cover, and this disposition allows of a communication between themselves, and a narrow passage between the plate and the cover. The copper tubes *ff*, fast in the cover, communicate with the narrow passage back of the plate *e e*, and carry the water which passes through the holes of the plate during the washing of the white lead.

Fig. 15.

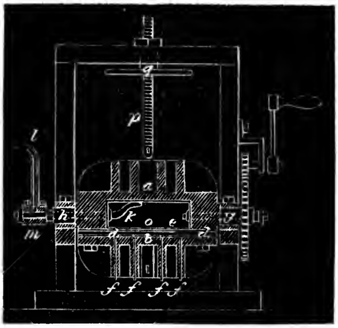


Fig. 17.

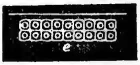


Fig. 16.

The receiver *a* is supported on the frame by two hollow trunnions *g*, *h*, lined with copper. *g* is closed with a plug during the operation, and *h* carries the tube *k*, which delivers the water brought by the tube *l*. *m* is the connecting stuffing-box. After the receiver is filled with white lead the cover is put on, and the apparatus is turned upside down by means of pinion and wheel gear.

A pump injects the water through *l* and *k* upon the surface of the white lead. and forces it through that substance and a filtering cloth *o*, spread upon the plate *e*. The water escapes from the holes of the plate into the narrow passage behind, and finally through the tubes *f f*. The washing should be continued until the water remains perfectly clear.

During this operation the white lead has been strongly compressed against the cover of the apparatus, and the water remaining above is run out through the plug hole *g*. The apparatus is then brought to its former position, the cover raised by means of the screw *p*, and the white lead removed.

11th. *Crompton Process.*

This process consists—

First. In purifying the gases obtained from bituminous coal burned by atmospheric air introduced in a peculiar manner;

Second. In washing the white lead in a solution of carbonate of soda, or any analogous chemical preparation, the proportions of which are indicated further on;

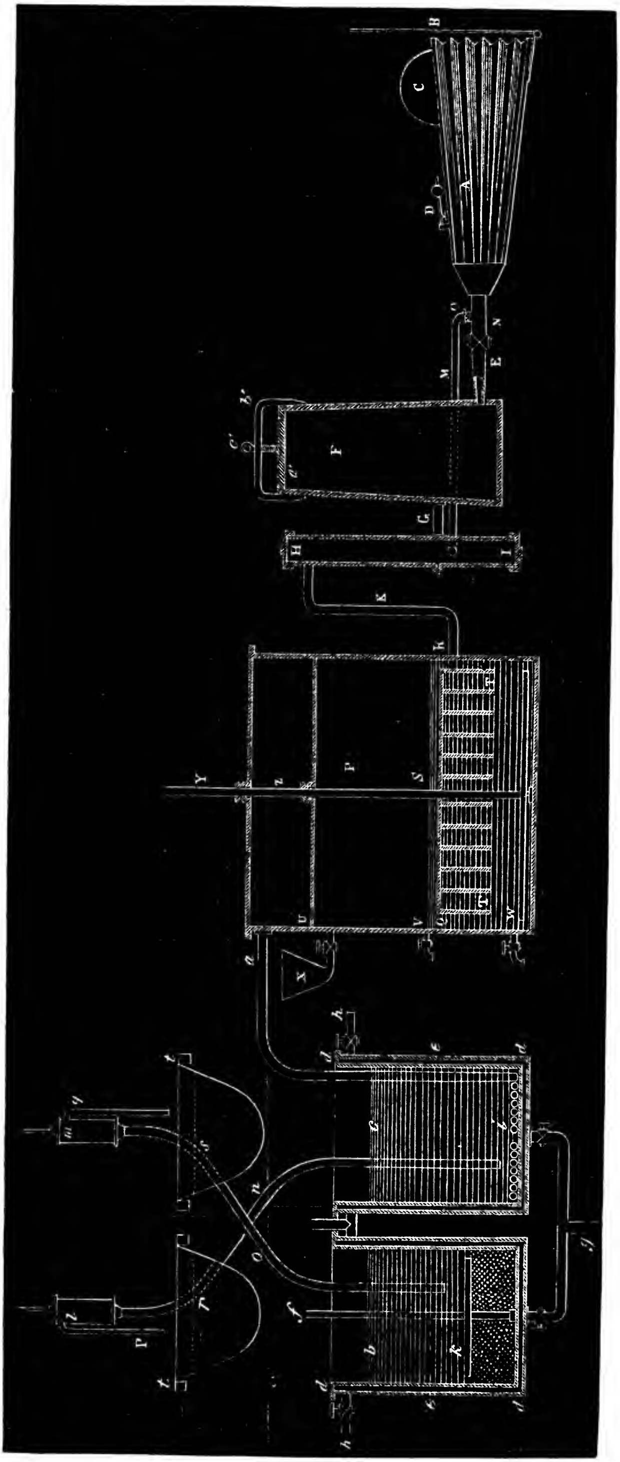
Third. In employing a basic nitrate of lead for the production of carbonate of lead;

Fourth. In using litharge, massicot, or any protoxide of lead, boiled with nitric acid or nitrate of lead, and exposing the hot solution to the action of carbonic acid;

Fifth. In condensing and purifying the carbonate of lead thus obtained by a simple, new, and economical method.

For these various operations we need: 1. A special apparatus for the production of white lead by means of litharge, massicot, or protoxide of lead, and this apparatus is provided with a pair of forge bellows, a safety valve, and other accessories; 2. A cylindrical cast-iron furnace with a cover of the same material, which is held by a screw and luted with clay, in order to prevent the access of the air; 3. A large cylindrical wrought-iron vessel which can be hermetically closed, and which contains a diaphragm of metallic gauze and a stirrer. The air or gases circulate through a conduit of a spiral form, and escape above by a central opening; 4. A copper pump for removing

Fig. 18.



the liquors from the various receivers, and forcing them upon cloth sieves disposed on top of other tanks; 5. Lastly, the other vessels, pipes, stopcocks, and accessories necessary for obtaining the gases, washing, and separating the carbonate of lead.

The following figures will explain the apparatus: In Fig. 18 A represents the bellows; B, the rod for operating it; C, a weight necessary to overcome the resistance of the air introduced into the furnace; D, safety valve, and E the tuyere.

F is the furnace composed of a cast-iron cylinder, stout enough for the purpose; *a′*, cast-iron cover which may be removed at will; *b′*, clamp fastened to the edge of the furnace, and through which passes the screw *c′* which compresses the cover against the clay luting put between it and the cylinder.

The flame passes through the cast-iron pipe G into the cast-iron cylinder H I, called *the flame receiver.*

K is a double-elbow pipe starting from the top of H I, which can be cleaned of ashes and dust through movable covers fixed on the top and bottom.

M is a branch pipe fixed at O on the tuyere E, and which, without passing through the furnace, carries the blast to the lower part of the flame receiver H I.

Fig. 19 shows the shape and direction of the pipe M, and the same letters answer for the corresponding parts of the previous figure. At N and O are stopcocks, the former on the tuyere and the latter on the pipe M, which has an area of one-fifth of that of the tuyere.

P is a large wrought-iron cylinder called *the washer*, which is tightly closed, and through which pass the gases of combustion. Q R is a disk carrying underneath it a spiral T T made of thin sheet iron, and communicating at R with the pipe K which delivers the hot gases. After circulating through the spiral, the gases escape through an opening in the centre of the plate Q R, and thence rise to the upper part of P.

Fig. 19.

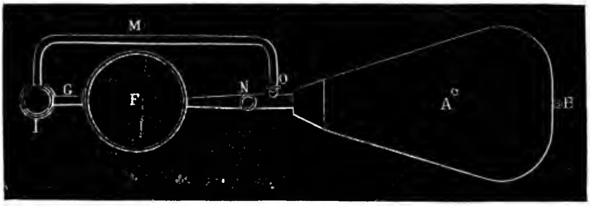
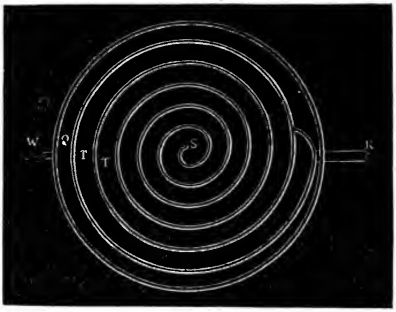


Fig. 20 is a horizontal section of the spiral T T.

Fig. 20.



The central opening through which the cooled and washed gases escape is shown at S.

U is a diaphragm of close metallic gauze, which is spread upon a perforated copper plate, and forms a complete separation between the upper and the lower part of P. V, W, stopcocks, and X funnel with a stopcock. Y vertical shaft of the stirrer passing through the stuffing-boxes Z.

The hot gases, after circulating through the spiral

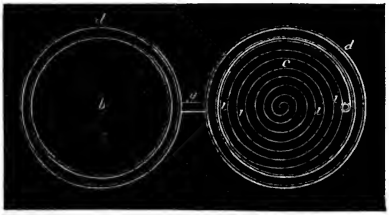
T T, escape at S, and traversing the diaphragm U, pass out at *a*.

b, *c* are copper receivers fitted with copper jackets *d d*, which leave between them the spaces *e e* for the circulation of the steam. *f*, pipe conducting the steam into those spaces. *g*, pipe for the escape of the condensed steam. *h h*, stopcocks for removing air.

The receiver *c* contains white lead, and *b* holds litharge.

i (Fig. 21) is a copper pipe forming a spiral at the bottom of the receiver *c*. One end of the coil is closed and the other is connected with the pipe *a*. It is perforated with a quantity of small holes which allow of the escape of the hot gases.

Fig. 21.



k is the horizontal arm of a stirrer placed in the vessel *b* holding litharge.

l, *m*, are copper pumps extracting the liquors from *b*, *c*, through the pipes *o*, *n* dipping into the apparatus. The liquors are then discharged through the pipes P, *q*, into the receivers *r*, *s*, after having traversed the cloth sieves placed on top, and spread upon the wooden frames *t t*.

Mode of working the Apparatus.—The cover of the furnace F is removed, and some burning charcoal is thrown in. The stopcock N of the tuyere is then opened, that at O remaining closed, and the blast is applied. After a while the furnace is charged with bituminous coal of the best quality.

When the fire is well lighted, the cover is luted down and fastened with the screw *c′*, and the stopcock at O is opened in order to complete the combustion of the fuel near the tuyere, before the gases are allowed to escape. In this manner the volatile portions from the fuel above the tuyere are forced to pass through the flame, where they are burned and decomposed before reaching the receiver H I.

The gases on arriving in this receiver are at a very high temperature, and find themselves brought in contact with another volume of air forced through the pipe M. This quantity of air is in such a ratio to that passing through the furnace, that the whole of the sulphuretted hydrogen is transformed into sulphurous acid and aqueous vapors. On the other hand, the carbonic oxide is converted into carbonic acid, and any combination of carbon and hydrogen becomes carbonic acid and water.

We should avoid passing through M more air than is needed, otherwise the temperature in H I will become lowered so much, that the decompositon of the sulphuretted hydrogen and of the hydrocarbons will no longer take place.

The blast being well regulated, we throw into the washer P five kilogrammes of carbonate of soda and the same weight of carbonate of lead, and through the funnel X we pour enough water to cover the plate Q R to the level of the stopcock V.

The receivers *b*, *c*, are then almost entirely filled with distilled water. In *b* we put twenty-five kilogrammes of litharge and ten of nitrate of lead, or any other quantity, provided, however, that this quantity of nitrate be $\frac{1}{30}$ of the weight of water held in the receiver.

Steam is admitted into the spaces *e e* of the jackets, until the contents of the vessel are boiling, and the stirrer *k* is made to revolve.

The rods of the plungers of the pumps *l*, *m*, are fixed upon a common axis which makes thirteen revolutions per minute. The pump *m* extracts the liquors from *b*, and delivers them to the filtering apparatus *s*, from which they flow into *c*; the other pump *l* takes the liquors from *c* with more or less suspended white lead, and after filtration at *r*, lets them fall into *b*.

Thus the air forced by the bellows passes through the furnace, and the hot gases of combustion pass into H I, thence by the pipe K through the washer P, thence again by *a* through the coil *i*, from which they escape in a multitude of bubbles into the receiver *c*.

By the succession of these various operations the white lead mixed with the liquors of *c*, is carried to the filter *r* upon which it is collected. The liquors *b* pass through the filter *s*, upon which they leave a certain proportion of undissolved litharge.

When the filters *r*, *s*, are entirely filled with white lead and litharge, they are removed and replaced by new ones.

With a furnace in constant operation, the charges are renewed every eight hours.

The stirrer in the washer P has a very slow motion, and the litharge in *b* should not be in such quantity as to prevent the free running of the stirrer *k*.

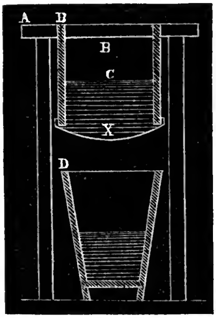
The water in P is always maintained at the level of V, and the dirty liquors from time to time removed at W, are replaced by fresh ones.

The liquors of *b* and *c* should occasionally be tried, in order to see whether any leakage takes place, or if they remain of a proper strength. If a sample of boiling liquor from *b* does not give on cooling, a precipitate of nitrate of lead, this substance is in insufficient proportion and more should be added.

After having described the apparatus and the various operations by which carbonate of lead is produced, it is now desirable to explain the processes of Mr. Crompton by which this substance is put into commercial shape, and the nitrate of lead mixed with the carbonate on the filter, recovered.

To the former apparatus already described, we add: 1. A square box B (Fig. 22), the bottom of which is formed of a close canvas filter X; 2. A large tub; 3. Another tub holding a vertical bronze shaft, provided with a series of blades slightly inclined, so as to divide the mass of carbonate of lead and compress it at the same time towards the bottom.

Fig. 22.



The substance on the filter *r* is placed in the box up to the level C, and fresh water is poured upon it to dissolve the nitrate of lead. The washing is continued until a sample of the filtered liquor ceases to become white by the addition of a solution of carbonate of soda.

All the washings are collected underneath in the tub D, and are afterwards used in the litharge receiver *b*. In this manner all the nitrate of lead is saved.

The washed white lead from the box B is thrown into the tub E (Figs. 23 and 24) holding the bronze shaft F with its inclined blades G G. By the motion of the stirrer the mass of carbonate of lead is made thoroughly homogeneous, and the separated water passes into the false bottom H through a cloth spread upon the perforated partition.

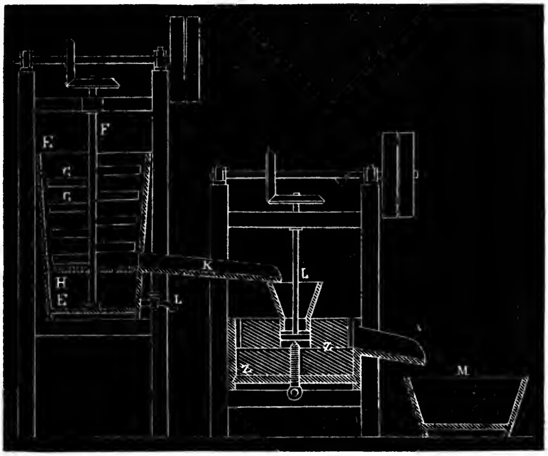


Fig. 23. Fig. 24.

The water is removed by the stopcock L, and the carbonate of lead is conducted by the inclined gutter K into the hopper L′, from which it is ground between the stones Z Z, to fall into the tub M. Lastly, it is formed into lumps and dried.

To sum up, Mr. Crompton claims the following points as new:—

I. The employment of carbonic acid and gases produced by bituminous coal, which is burned in such a manner, by a peculiar introduction of air, that the vapors which otherwise might injure the quality of the product are destroyed.

II. The manufacture of white lead by a mixture of nitric acid and oxide of lead, in such proportions that there be an excess of oxide; or by keeping at the point of ebullition a mixture of litharge, massicot, or any oxide of lead, with a solution of commercial nitrate of lead. A pure carbonate of lead is obtained by passing a stream of carbonic acid through these hot solutions.

III. The constant recovery of the nitric acid or nitrate of lead employed, serving for fresh additions of litharge.

IV. The purification of the carbonate of lead by successive washings, which were not practised before the above process was invented.

Mr. Crompton, since his patent of September 7th, 1838, has obtained other certificates of improvements of the dates of February 6th and July 18th, 1839.

The improvements of the patent of February 6th, 1839, are:—

1. The employment of anthracite, coke, and any other carboniferous substances, instead of charcoal generally used for the production of carbonic acid. Also, the purification of the gases of the combustion, and the destruction of the vapors which may injure the purity of the carbonate of lead. This purification is done as follows:—

By a second combustion effected, as we have already seen, in a flame receiver by means of a new addition of atmospheric air. The combinations of sulphur, carbon, and hydrogen, are thus transformed into water and carbonic and sulphurous acids.

By condensing the sulphurous acid and the still remaining sulphuretted hydrogen, in solutions holding neutralizing substances.

2. The use of the nitrate of lead, instead of the acetate, hitherto employed.

3. The proper degree of temperature necessary to keep in solution the basic nitrate of lead, which is very slightly soluble in the cold.

This improvement is not limited to the foregoing combinations: the mode of preparing carbonic acid is equally good whether we employ the acetate or the nitrate of lead. We may also use the nitrate of lead in connection with carbonic acid made from charcoal, and produce the carbonate of lead in hot solutions, whatever be the acid employed.

Lastly, the precipitation of the carbonate of lead in hot liquors, has a great effect on its mode of aggregation.

The first patent indicates hot solutions of nitric acid or of nitrate of lead as solvents, and the purification of the carbonic acid whatever be the solvent employed.

The last patent of July 18th, 1839, comprises the heating of the lead solutions during their preparation, as well as during their precipitation by carbonic acid. The solvent is acetic acid or the acetate of lead.

The temperature should be about 60° C., or a little above. The solution is composed as follows:—

Pure acetate of lead or its equivalents in oxide of lead and acetic acid	10 parts.
Litharge (oxide of lead)	25 "
Water	200 "

These proportions may vary somewhat, however.

12th. *Gannal Process.*

This process consists:—

1. In granulating the lead;

2. In reducing the granules to a finer degree of comminution by mutual attrition in a leaden cylinder;

3. In oxidizing the metal by the introduction of air into the apparatus;
4. In carbonating the oxide with a mixture of air and carbonic acid;
5. In aiding the oxidation by an addition in the apparatus of nitric acid or nitrate of lead;
6. In washing the product thus obtained;
7. In hastening its desiccation by a previous pressure which expels most of the water;
8. In dividing the pressed paste into square blocks;
9. In drying these blocks in a stove-room.

This process has been improved by Mr. Versepuy, as we have already seen.

13th. *Rostaing Process.*

Mr. de Rostaing, in 1858, proposed for the manufacture of white lead and massicot a process based upon the pulverization of metals submitted, when melted, to centrifugal action. A continuous stream of molten lead falls upon a metallic disk, 0.25 metre in diameter, making a maximum of 2000 revolutions per minute, and is projected with great force tangentially to its circumference. Four or five minutes are sufficient to thus pulverize about 100 kilogrammes of lead. The fine metallic powder, being still hot, is rapidly oxidized in its passage through the air, and may be converted into massicot or red lead, or may be combined with carbonic acid. This process has not been put into practice.

14th. *Mulhouse White Lead.*

This is a combination of sulphuric acid and oxide of lead, being the residue of the manufacture of acetate of alumina. It is thoroughly washed with water, passed through a silk sieve, and drained upon cloth filters. It is afterwards moulded in the shape of a truncated cone, and dried. This product, misnamed white lead, cannot be used for oil painting, since it has no body—does not cover. We mention it because it is frequently employed for adulterating real white lead.

This sulphate of lead may by transformed into carbonate by boiling it with a solution of carbonate of soda or of potassa. But this operation renders it more expensive than real white lead, and the product is still contaminated with a certain proportion of sulphate of lead.

15th. *Silver White or Light White.*

This white, often employed for decorating and for artistic painting, is a white lead of the first quality which has been peculiarly well washed.

A superior quality of silver white for delicate oil painting may be obtained by dissolving 500 grammes of acetate of lead in 2 litres of boiling water and diluting with 4 litres more of water. Then a solution of 370 grammes of soda crystals in 2 litres of boiling water, is slowly poured into the former liquors, stirring all the while. The two mixed solutions are allowed to settle for two hours, when the supernatant liquid is decanted. The precipitate is washed five or six times by decantation, then drained upon a cloth, and dried in the dark at a gentle heat.

16th. *Testing the Purity of White Leads.*

We should carefully avoid mixing with white lead substances which may impair its brightness, since a pure white is its main quality. We shall see further on what its composition is.

White lead should be kept in closed vessels, otherwise it will acquire a brown shade. It forms the basis of a great many pigments. It should, for good paintings, be pure and without admixtures ; however, house painters add to it variable proportions of chalk or Meudon white, but the painting is without consistency or durability. Here is the process indicated by Watin for distinguishing white lead from chalk. A hole is made in a piece of charcoal, which is then ignited and a pinch of white lead thrown in. Air is blown upon the charcoal in order to keep up the combustion, and the white lead first turns yellow, and after a few minutes becomes reduced to bright globules of metallic lead. Chalk (carbonate of lime), on the other hand, may lose its carbonic acid by the operation, but the lime will remain as a white powder upon the charcoal.

If we desire to ascertain the proportion of carbonate of lime mixed with the carbonate of lead, we weigh 100 grammes of the sample, and mix them with 50 grammes of charcoal powder. The whole being smelted in a crucible, a button of metallic lead is produced, which is weighed. We then add 24 per cent. to the number obtained, and subtracting this sum from the previous 100 grammes, the difference is the weight of the carbonate of lime. The 24 per cent. represent about the weight of the carbonic acid, water, and oxygen separated from the carbonate of lead.

These two tests would be sufficient if carbonate of lime were the only foreign substance of the mixture. But as sulphate of lead may also be present, we are obliged to employ tests by the wet way. For instance we put 25 grammes of the sample into a glass flask, and pour gradually upon it nitric acid diluted with six times its weight of water. The acid is added as long as an effervescence takes place, and we heat the vessel gently. If all the substance be dissolved, we conclude that there is no sulphate of lead. Should there be an insoluble deposit, we throw the whole upon a filter and wash it thoroughly. The sulphate of lead collected is then dried and weighed. Let us suppose that its weight is 7 grammes. The filtered liquor contains chalk and the dissolved white lead; their separation is effected by adding ammonia until the liquor smells of it slightly. The precipitate of oxide of lead is collected upon a filter, washed, dried and weighed. Let the supposed weight be 10 grammes; we know that 100 parts of oxide of lead are equal to 119.78 parts of white lead; therefore 10 grammes of oxide represent 11.978 grammes of white lead, that is, 12 grammes without fractions. Deducting from the 25 grammes of sample the sum of the weights of sulphate and carbonate of lead, there remain 6 grammes of carbonate of lime. Lime may be ascertained and determined by pouring into the liquor, filtered from the oxide of lead, a solution of oxalate of ammonia which will produce a white precipitate of oxalate of lime. The results are only approximate, as we do not wish to complicate the operations which require a certain amount of chemical knowledge in order to operate with certainty. We have also found samples of white lead which were mixed with sulphate of baryta or clay; these substances remain in the insoluble residuum.

Here are the processes employed by Mr. Louyet for ascertaining the impurities of white lead:—

"I was intrusted, some time since, with three different samples of white lead, intended for exportation. It is probable that the destination of these products induced the manufacturer to think that it was useless to remain within bounds, and that the ignorance of the consumers would prevent them from ascertaining that what was sold as white lead could be as properly called sulphate of baryta as white lead.

"One gramme of sample No. 1, heated to redness in a platinum crucible until complete transformation into oxide of lead, gave a loss of . 0.100 gramme.

"A second calculation gave the same weight.

"For one gramme of sample No. 2, calcined in the same manner, the loss was . . . 0.049 gramme.
"Sample No. 3, 1 gramme, loss . . . . 0.037 "

"The calcined product No. 1 was boiled with pure nitric acid, then water was added and the boiling continued. The insoluble residuum was yellowish, although the liquor was strongly acid. After filtration the residue was well washed with boiling water and calcined. Its weight was 0.305 gramme after deducting the ashes of the filter.

"I will observe that the residuum of No. 1 was darker than that of No. 2, and this latter darker than No. 3, which was quite white. The residuum of No. 1, after being heated with the blowpipe upon charcoal and with soda, stained a permanent black the piece of silver upon which it had been put wet.

"This is a characteristic of sulphates. It was proved that the sulphate mixed with the carbonate of lead was sulphate of baryta, by boiling it with a solution of carbonate of soda, filtering, and dissolving the washed residue upon the filter with hydrochloric acid. The liquor obtained gave a heavy white precipitate with sulphuric acid.

"The solution resulting from the treatment of white lead No. 1 with nitric acid was precipitated with sulphuric acid, and the calcined sulphate of lead weighed 0.765 gramme, corresponding to 0.563 gramme of oxide of lead, or 0.674 gramme of neutral carbonate. Calculated from the proportion of oxide of lead, that of carbonic acid is 0.111 gramme, whereas the loss by calcination of the white lead is only 0.100 gramme. I admit that this difference is due to the fact that all of the oxide of lead is not carbonated, but that a certain proportion remains in the hydrated state. But, as the equivalent of water is smaller than that of carbonic acid, it follows that the number is too high if we suppose that all of the oxide is combined with carbonic acid, and we must subtract 0.011 from 0.674; there remains 0.663 gramme. White lead No. 2 was treated in the same manner, and the residue insoluble in nitric acid weighed 0.660 gramme after being washed and calcined. The proportion of sulphate of lead from the nitric solution was 0.360 gramme, corresponding to 0.264 gramme of protoxide of lead. But here the number calculated for carbonic acid differs but little from that found by direct experiment. In this case, as in the former, the number obtained for carbonate of lead is a little low, and the loss may be added to it. Indeed, the sulphate of lead is slightly soluble in acid liquors, and the precipitation by the oxalate of ammonia would have given more accurate results. It follows that the calculated number for carbonic acid would have been a little higher, and above that found by direct experiment.

"But I repeat the observation already made, that a portion of the oxide of lead in white lead is in the hydrated state. One gramme of the sample No. 3 gave an insoluble residuum equal to 0.718 gramme, and a precipitate of sulphate of lead weighing 0.277 gramme, which corresponds to 0.203 of oxide of lead or 0.243 of carbonate of lead.

"The composition of the samples was, therefore, as follows:—

	White lead.	Sulphate of baryta.
1 gramme sample No. 1 . . .	0.695	0.305
1 " " No. 2 . . .	0.340	0.660
1 " " No. 3 . . .	0.282	0.718

"These analyses, the last one especially, show that I was right in saying that these products may indifferently be called white lead or sulphate of baryta."

White lead is often mixed with that sulphate of baryta which is called *blanc fixe* or *baryta white*, and which is prepared from the carbonate of baryta. It is an adulteration which ceases to be objectionable when the manufacturer makes the composition known.

Belgian and German manufacturers sell various qualities of white lead, the compositions of which are known by the names they bear; thus:—

1. Krems white is a pure white lead;
2. Venice white is a mixture of equal parts of sulphate of baryta and white lead;
3. Hamburg white is a mixture of—

Sulphate of baryta	2 parts.
White lead	1 part.

4. Holland white is composed of—

Sulphate of baryta	3 parts.
White lead	1 part.

A bluish tinge is often imparted to white lead with a small proportion of indigo.

It is said that the following mixtures are generally found in the French color trade:—

	White lead.	Sulphate of baryta.
White lead (superfine) . . .	85	15
No. 1 . . .	70	30
No. 2 . . .	60	40
No. 3 . . .	40 to 50	60 to 50

In order to ascertain whether a sample of white lead is mixed with sulphate of baryta or sulphate of lead, it is treated with nitric acid diluted with two or three parts of distilled water. Pure white lead is entirely dissolved, whereas the above sulphates remain unacted upon by the reagent.

Mr. A. Bacco has indicated a simple process by which white leads may be tested by the wet way.

"The quality of white leads," says he, "as every chemist knows, depends on their extreme opacity, which is the greater as their molecules are amorphous and their composition more basic. In experimenting upon a crystalline white lead, with little body, I have ascertained that it may be improved by digesting it in a carbonated alkaline solution, rendered slightly caustic by an addition of a small quantity of quicklime. The entire operation is performed in the cold.

"But as a white lead should be basic, in order to have body, I have tried a process for ascertaining whether a white lead is more or less basic, and I have succeeded with a solution of neutral chromate of potassa poured upon wet white lead. This latter substance is converted into a chromate of lead, which is neutral, basic, or six basic, according as the white lead itself is more or less basic, and the degree is shown by a change of coloration.

"If the chromate be lemon-yellow, the white lead is neutral and of inferior quality; an orange color indicates a white lead slightly basic, but if the color be a scarlet-red we may be sure that the white lead is highly basic. Indeed, every chemist knows that the neutral chromate of lead is lemon-yellow, the tribasic orange-yellow, and the six-basic fire-red.

"We may then conclude that the degree of coloration thus obtained gives a sure indication of the quality of white leads."

All these methods of ascertaining the purity of white leads appear to us far from entirely satisfactory; and, by reading the following paragraph, it will be seen that the composition of this product is not so simple as is supposed, and that a thorough chemical analysis will alone give correct indications of the quality of white lead.

17th. *Composition of White Leads.*

Mr. Mulder, of Utrecht, has published the results of experiments made by Mr. Vlaandern upon the composition of twenty-seven samples of white lead of Holland manufacture. The results are sufficiently interesting to be reproduced here. In the analyses the hygroscopic water has not been determined separately.

	I.	II.	Calculated.		Equivalents.
CO^2	11.4	11.4	11.4	=	2
HO	2.3	2.4	2.3	=	1
PbO	86.4	86.5	86.3	=	3

or

$$PbO,HO + 2CO^2,PbO.$$

	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	Calculated.	Equivalents.
CO^2	12.4	12.2	12.0	12.4	12.0	12.3	12.3	12.0	12.3	12.2	12.2	= 5
HO	2.0	2.1	2.0	2.1	2.0	2.1	2.3	1.8	2.1	2.0	2.0	= 2
PbO	85.0	85.6	85.9	85.7	86.1	85.4	85.5	85.6	85.5	85.6	85.8	= 7

or

$$2PbO,HO + 5CO^2,PbO.$$

	XIII.	XIV.	XV.	XVI.	XVII.	XVIII.	XIX.	Calculated.	Equivalents.
CO^2	12.7	12.7	12.5	12.7	12.5	12.9	12.9	12.7	= 3
HO	2.3	1.7	2.1	1.9	1.9	1.2	2.1	1.7	= 1
PbO	85.2	85.5	85.8	85.4	85.7	85.3	85.1	85.6	= 4

or

$$PbO,HO + 3CO^2,PbO.$$

	XX.	XXI.	XXII.	XXIII.	XXIV.	XXV.	XXVI.	XXVII.	Calculated.	Equivalents.
CO^2	13.1	13.5	13.5	13.2	13.0	13.3	13.2	13.1	13.4	= 4
HO	2.0	1.5	1.6	1.7	1.8	1.8	1.9	2.0	1.4	= 1
PbO	83.4	84.7	84.9	85.2	85.2	85.1	85.0	85.1	85.2	= 5

or

$$PbO,HO + 4CO^2,PbO.$$

Thus, the samples of white lead which were examined had the following compositions:—

Two, $PbO,HO + 2CO^2,PbO.$
Ten, $2PbO,HO + 5CO^2,PbO.$
Seven, $PbO,HO + 3CO^2,PbO.$
Eight, $PbO,HO + 4CO^2,PbO.$

Therefore, Holland white lead is a hydrated oxide of lead with 2, $2\frac{1}{2}$, 3, or 4 equivalents of neutral carbonate of lead. 2 and 3 are met with in the trade not so frequently as $2\frac{1}{2}$ and 4.

Mr. Mulder regrets that he does not know the manufacturers by whom these products were made, because he would then have been able to ascertain whether the white lead of a given manufacture preserved the same composition.

On the other hand, Mr. W. Baker has demonstrated that white lead made by the Holland process has no fixed composition, but that it is a carbonate of lead holding a variable proportion of hydrated oxide, which depends on the conditions attending the corroding process. Thus, from the same bed, using the same tan and acetic acid, samples may be taken presenting variable proportions of carbonate and hydrate of lead. Near the walls, where the aqueous and carbonic vapors escape freely, there are sometimes found, under certain circumstances, small translucent crystals of neutral carbonate with a sweet taste. On the corroding surface there is often seen a thin crust, the composition of which is nearly that of the neutral carbonate. The quantity and the quality of the water employed in grinding and washing white lead have also an effect on the composition of the product. Here are a few analyses of dry white lead from various manufacturers, which quite agree with those of Mr. Mulder.

		No. I.	Calculated.		Equivalents.
CO^2		11.03	11.4	=	2
HO		2.23	2.3	=	1
PbO		86.11	86.3	=	3
		No. II.			
CO^2		12.17	12.7	=	3
HO		1.66	1.7	=	1
PbO		85.37	85.6	=	4
	No. III.	No. IV.			
CO^2	13.37	13.48	13.4	=	4
HO	1.11	1.46	1.4	=	1
PbO	84.71	84.88	85.2	=	5

The hygroscopic water does not generally amount to more than 0.05 per cent.

The white lead No. I. was from London, No. II. from Newcastle, and Nos. III. and IV. from Sheffield.

Moreover, what still demonstrate the variety in the composition of white leads are the following analyses of crusts separated from the leads:—

	CO^2.	HO.	PbO.
No. 1. Solid crust of good quality . .	12.49	1.60	85.24
No. 2. " " " " . .	12.31	1.73	85.77
No. 3. Crust with scaly surface . . .	15.14	0.53	83.86
No. 4. Hard crust, not very deeply corroded	15.14	0.60	84.10
No. 5. Colorless, crystalline, and tranlucent crusts	15.71	0.75	83.53
No. 6. Colorless and crystalline crusts taken from a mass sweet to the taste . . .	16.11	0.49	83.39
No. 7. Neutral carbonate, calculated . .	16.50		83.50

It is evident that Nos. 5 and 6 are neutral carbonate with a trace of hydrate, and that Nos. 3 and 4 show the passage from the neutral carbonate to the normal corroded product, the composition of which may be represented by the formula—

$$PbO,HO + 3CO^2,PbO.$$

18th. *Processes for Rendering the Manufacture of White Lead less Unhealthy.*

The manufacture of white lead presents various manipulations which are quite unhealthy, because of the continual handling of a poisoning substance, and especially of the white lead dust flying about the work-rooms and being inhaled by the men.

The cause of humanity before all, and possibly an economy in the manufacture, demand of us to search for the means of diminishing the danger. It is only of late that this question in public hygiene has been brought into serious consideration, and has been successfully resolved. We owe much in this respect to the exertions of the "Société d'Encouragement," and we shall borrow from its bulletin a few interesting documents which relate to successful improvements carried into this manufacture.

A. *The Ward Machine for the Manufacture of White Lead.*

In order to appreciate, at its real value, the invention of this machine, we should remember that white lead is a powerful poison, which, by the ordinary processes, is reduced into a very fine dust, penetrating the pores of the skin, the respiratory organs, and the lungs. Thus, the clothes of the men working in such a manufacture are constantly impregnated with this impalpable powder, in the same manner as those of millers are with flour.

The health of these poor men is soon seriously impaired, their complexions become livid, and they soon fall into a state of languor and consumption, produced by inflammation of the viscera.* In a few years they decay and die before the time nature had allotted to them.

It is, therefore, a great humanitarian service to endeavor to preserve from death so many men working in this dangerous manufacture, and Mr. Ward thinks that he has attained this great result, which, however, has also attracted the attention of Messrs. Schuzenbach and Gannel.

His apparatus comprises:—

I. A trough, 4 metres long, 2 metres wide, and 1.30 metres deep.

II. Two brass rollers, superposed, for grinding the substances. The lower one is entirely immersed in water, and the upper one partly so, their line of contact being 30 centimetres below the level of the water. Motion is imparted to them by means of a

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* In the autopsy of men from white lead works, lead was always found attached to the viscera. There was, therefore, no doubt of their premature death and of the cause of it.

crank or pulley, fixed to the axis of the upper cylinder, which is connected with the lower one by pinions.

Counterweights are also fixed to the extremities of the upper axis, giving a sufficient pressure, and, at the same time, allowing an upward motion of the cylinder, should too great a mass of metal become engaged between the rolls.

III. An oaken platform, perforated with a quantity of holes, 15 or 16 millimetres in diameter, and serving as a sieve for the material which leaves the rolls. This platform is maintained at about 8 centimetres below the rollers by means of wooden blocks (holdfasts) above and below it.

IV. A wooden inclined plane for feeding the rollers.

An outlet is left on one side of the trough for the water. The white lead, which is quite finely pulverized, falls easily through the holes of the platform, whereas the laminated metal remains on top and is raked out.

As the non-corroded metal is separated from the white lead entirely under water, no dangerous dust can be raised.

Lastly, the metallic plates are allowed to drain upon an inclined trough, and to become dry before they are used or melted anew.

"It may be inquired," says the inventor, "why the substances are not wetted before passing through the rolls. The answer is this:—

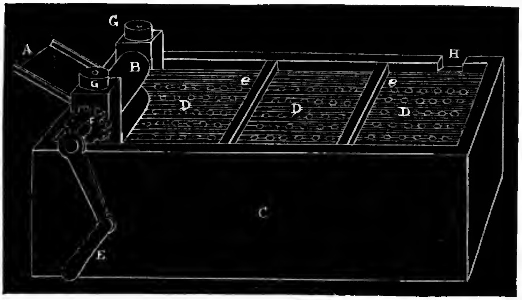
"1. They would become pasty, and their passage through the rolls be difficult.

"2. This paste would not be well sifted.

"3. A certain proportion of metallic lead is necessary to the operation, and should not be removed before the substances are passed through the cylinders."

Fig. 25 shows the apparatus, which has been already explained.

Fig. 25.



A, inclined plane for feeding the rollers.

B, the superposed brass rollers for grinding the substances.

C, wooden trough.

D, oaken partition perforated with holes.

E, crank, here indicated as a means of imparting motion. It can be substituted by pulleys, for instance, driven by water or steam power.

F, pinion fixed to the axis of the upper cylinder, and driving the lower one.

G G, two counterweights bearing upon the axis of the upper roller.

H, water outlet.

B. *Apparatus of Mr. Th. Lefèvre for Pulverizing White Lead.*

Mr. Th. Lefèvre, manufacturer of white lead at Lille, patented, in 1849, an apparatus for grinding white lead, the description of which is as follows:—

"The ordinary process for pulverizing white lead blocks consists in grinding them between two horizontal stones, the upper one of which is revolving. The powder is then sifted in order to separate the coarse portions. This mode of operation, whatever be the precautions taken, is open to the objection of producing in the works a very light dust of white lead, which is inhaled by the men and produces that dangerous sickness called lead colic.

"We have tried to replace this dangerous method by one presenting no cause of insecurity to the men, and we have succeeded by the use of an apparatus actually in operation in our own works.

"Instead of working two horizontal stones in the open air, we keep them in a tight inclosure. The lower stone is steady, whereas the upper one revolves and receives its motion from a vertical shaft passing through the middle of the lower stone, and fixed to a three-branched rynd in the upper one. A copper cover screwed upon the casing of the stones, supports the distributor of white lead. This distributor is made of two truncated cones, one of which, the exterior, is bolted upon the copper cover. The interior one is fixed to a vertical revolving shaft. Both cones are cast with grooves in opposite directions.

"The lumps of white lead are first reduced in size in the distributor, then finely powdered between the stones, and lastly, sifted in sieves kept in hermetically closed boxes.

"Fig. 26 is a vertical section of the apparatus passing through the line A B C D (Fig. 27).

"Fig. 27 is a horizontal section passing through the line E F G H (Fig. 26).

Fig. 26.

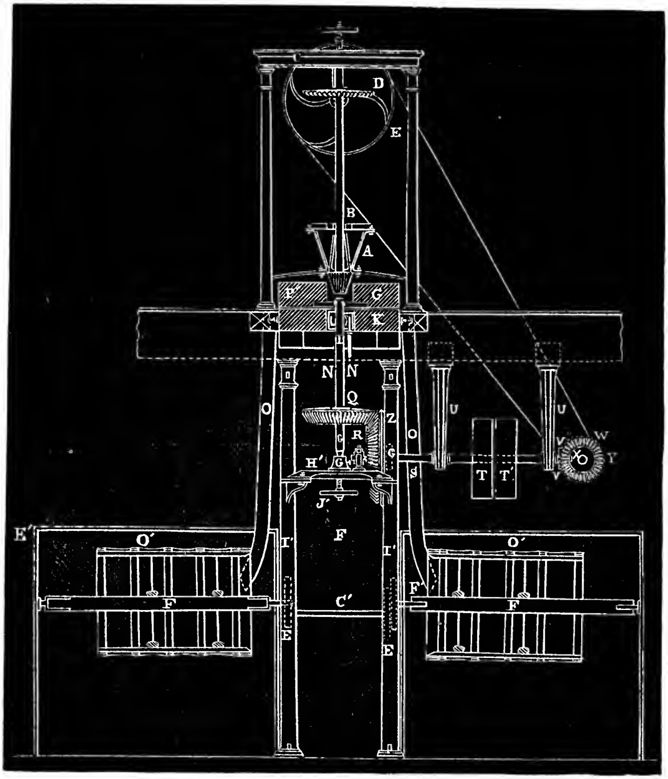
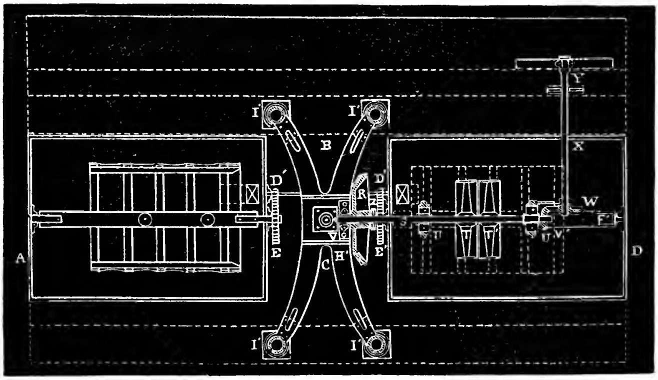
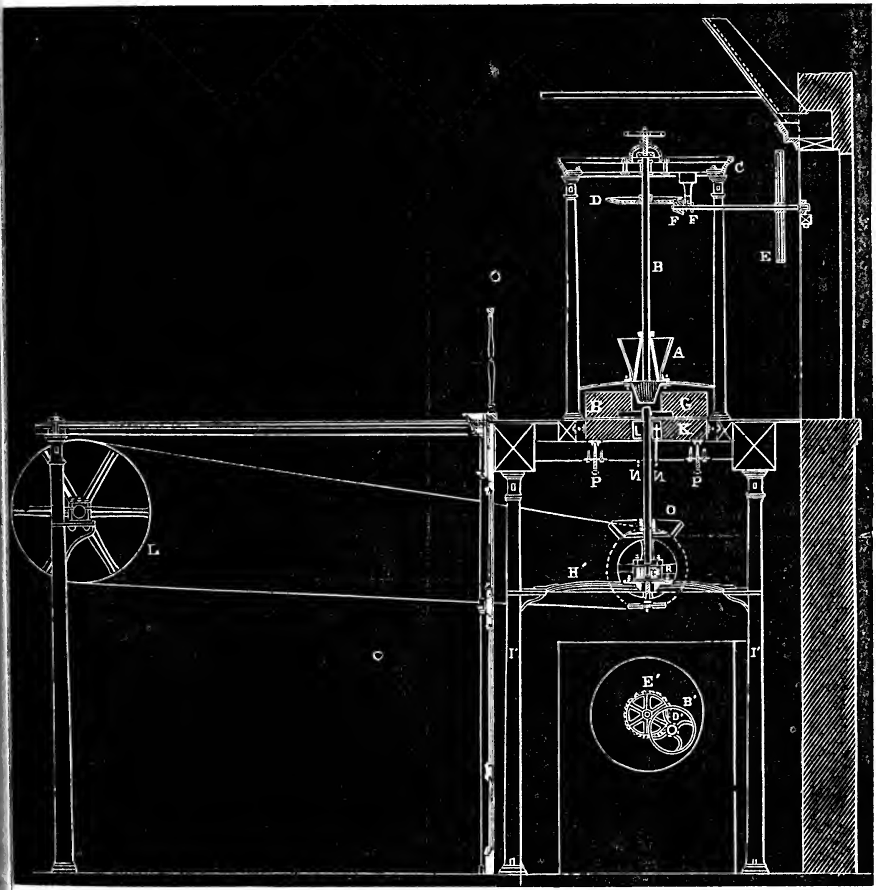


Fig. 27.



"Figs. 28 and 29 represent another transverse and vertical section of the apparatus.

Fig. 28.

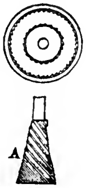


“ Fig. 30 is the distributor on a larger scale.

“This distributor is made of cast-iron and is lined inside with a bronze casting filled with grooves. Another grooved cone A revolves inside, and breaks the lumps or blocks of white lead into small fragments, which fall between the stones G K.

“B, vertical iron shaft, fixed to the small distributing cone, and rising up to the capital C, on top of which there is a screw

Fig. 30.



which allows of the raising or lowering of the shaft, in order to regulate the delivery of the white lead to the stones G K.

“C, cast-iron capital supported by four columns, and which maintains the vertical shaft in its bearings.

“D, F conical gearing driving the shaft B by means of the pulley E, fixed upon the horizontal shaft F′.

“G, upper stone of white marble, which could be substituted by a burr-stone. A three-branched rynd is fixed in the central opening, and receives the shaft I. The under surface of the stone (Figs. 31 and 32) has three grooves or ways J J J for delivering the pulverized white lead.

Fig. 31.

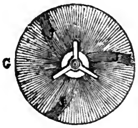
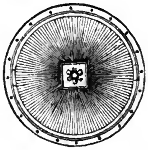


Fig. 32.



“K, lower steady stone of the same material as the upper one and grooved. It is perforated in the centre with a square hole which is filled with a box L of iron on the sides, and copper on the top.

“This box is divided into six compartments, three for the grease and three for the brasses. The latter are regulated by the screws N N N. Three or four screws P P maintain the level of the stone.

“The stones are supported by a framework upon which is screwed a hermetical copper cover, bearing the distributor of the white lead.

“Between the stones and their casing there is an empty space P′, which receives the projected white lead. Two opposite openings deliver it into the rectangular zinc spouts O O, which, in their turn, conduct the pulverized material into the revolving sieves O′ O′, held in hermetically closed boxes. These sieves are a check on the neglect of the men, because the stones, when properly set, grind well enough without the necessity of sifting.

"Q R, conical gearing driven by the fixed pulley T. T′ is a loose pulley.

"U U, brackets supporting the shaft S.

"V W, conical gear driving a pulley Y fixed upon the shaft X, and transmitting its motion to the pulley E of the distributor.

"Z, pulley on the shaft S driving the two sieves O′ O′ by means of the pulley and pinions B′ D′ E′.

"The shaft of the revolving stone stands upon a cast-iron or steel step G′ fixed upon cross-bars H′ bolted to the four columns I′.

"J′, screw under G′ for raising or lowering the upper stone G.

"K′, main driving shaft upon which are fixed the pulleys L′."

Mr. Th. Lefèvre has not only invented the above described apparatus, but he has since organized his works on an entirely salubrious system of manufacture. We cannot describe it better than by presenting the report made by MM. Barreswill, Salvétat, and Chevalier to the "Société d'Encouragement."

The works of Mr. Th. Lefèvre, founded in 1825, have since then received many improvements. A steam-engine of thirty horse-power gives motion to all the machinery of the works. Several small railroads carry the crude or prepared materials in every direction, and are a great saving of arduous labor.

Gas is manufactured in the place, and is used from

120 burners. The stack of the gas furnace is 33 metres high. The retorts are made of clay, and the cracks are closed with a mixture of powdered glass, borax, and pipe clay.

There are from eighty to one hundred and twenty men employed in the works, the smaller number in dull times. Mr. Lefèvre produces yearly from 1,600,000 to 1,800,000 kilogrammes of white lead thus subdivided:—

White lead in scales from	45 to 50,000	kilogrammes
“ “ lumps “	300 “ 350,000	“
“ powdered “	1100 “ 1,200,000	“
“ ground in oil “	150 “ 200,000	“

The consumption of the latter article increases daily and its manufacture follows the progression.

The good quality of the products of these works has been acknowledged in the national exhibitions, and at the World's Fair, London.

The mode of manufacture is the Holland process, and we shall successively describe the operations which we have seen practised.

Casting of the lead.—This operation is effected in a special room called the foundry, and the lead employed is either new metal or that which has not been entirely corroded. In the latter case certain precautions are taken to protect the men from the vapors produced during the fusion. Thus the metal is put through front sliding-doors, into a cast-iron kettle entirely covered with a hood, the top of which communicates by means of a pipe, with the stack of the furnace, 12 metres high, and having a strong draft.

Before being put into the kettle, the lead is for some time kept in a hot place, where all dampness is removed. Thus is avoided the danger of the molten metal being thrown out, as when wet lead is introduced into a fused bath.

When the lead is melted, it is cast into sheets about 60 centimetres long, 10 wide, and a few millimetres thick, and weighing 1 kilogramme on an average. These sheets are then carried into another and adjoining room, where they are cut in two and rolled into the shape of a spiral which fills the pots of the beds.

These operations present none or very little danger. In nineteen years, a single melter only has suffered from lead disease.

Building the beds.—There are forty-eight beds at the works of Mr. T. Lefèvre at Moulins-Lille. They are stone built, and begin at 1 metre below the level of the ground. Their dimensions are 5 metres long, 4 wide, and 6 high.

Stable manure is employed, but other works use spent tan. In the latter case the operation is slower, and requires from sixty to ninety days, instead of forty, as with stable manure.

A banquette, 30 centimetres wide and 40 high, is built around the bed with the manure from a preceding operation, while the middle is filled with a layer of fresh manure 40 centimetres high. This first layer receives about 1200 pots, into each of which there is poured about a fourth of a litre of vinegar. A spiral of lead is then put into each pot, and rests upon two inside knobs which prevent it from touching the vinegar.

The whole is then covered with flat leaden sheets, then with pieces of scantling from 10 to 12 centimetres square, in order to leave room for a draft, and lastly with boards. Another banquette of old manure is formed upon the first layer, and the middle space is filled with fresh manure. Pots, vinegar, and lead are arranged as previously explained, and the building up of the bed goes on until there are seven or eight layers.

In about six weeks the conversion of the lead into carbonate is complete, or nearly so.

On an average, each bed requires—

1. 8 two-horse loads of stable manure;
2. 300 litres of vinegar per layer, or 2400 per bed;
3. 1200 to 1500 kilogrammes of lead per layer, or from 10,000 to 12,000 kilogrammes per bed.

Four men build two layers per day, or a bed in four days: that is, sixteen days work per bed.

There is no insalubrity in the building of the beds. Gas-burners may be used when desired.

Taking the beds apart.—When the time necessary for the corrosion of the lead has expired, the beds are taken apart in the following manner: The manure, boards, and pieces of scantling of the top layer are removed. The corroded lead is then emptied into a small wooden box, and the largest portions of uncorroded metal are picked apart. There must be a little dust produced, but the testimony of many workmen is that this operation is attended with very little danger to health. In another establishment at Lille, the men are allowed to smoke when taking the beds apart, and the manager certifies that many cases of sickness are thus prevented.

In Mr. Woelmann's works the lead from the beds is never melted anew; the uncorroded portions are used for covering the pots.

12,000 kilogrammes of lead give on an average: First, carbonated lead 10,000 kilogrammes; second, non-corroded lead 4000 kilogrammes. Therefore, the increase of weight of the 8000 kilogrammes of lead which are corroded is 25 per cent.

The taking apart of the beds is done with naked hands. Gloves are not very handy to work with unless they are very supple, in which case they become expensive.

Picking up.—Before 1842 the white lead from the beds was carried to the picking room, where the carbonate was separated from the metal. As this operation requires the beating and unrolling of the sheets, it is very unhealthy on account of the great quantity of flying dust. Strong drafts kept in the room were insufficient as a preventive of danger, and were attended with loss of material. Moreover the operation was slow.

The separation of the white lead from the uncorroded metal is now effected in Mr. Lefèvre's works by a special machine, kept separate in a tight enclosure. This machine is on an upper floor, 3 metres above the ground. The metal, with the adhering white lead, is carried by an endless leather apron to a series of two pairs of grooved rollers, which separate the greater part of the white lead. The remainder is removed by the friction of the metal in a revolving drum, covered by metallic gauze. The white lead is received into a large closed box. The portions of blue lead which are sufficiently large are rolled up into spirals for the pots, whereas the small fragments are melted anew.

As soon as the dust has subsided, the white lead is removed from the receiving box.

Dry grinding of scales of white lead.—Formerly the scales separated from the metal were ground under vertical running stones, and the product was sifted, what passed through the sieve being mixed with water and then ground under horizontal stones.

At the present time the scales are carried by mechanical means to the first story, and fall into large troughs, from which they are taken to a hopper provided with a distributor. The scales pass first between two grooved rollers, which break them and separate the blue lead still remaining. Three other pairs of rollers bring the white lead to the proper degree of comminution for the wet grinding. All this work, which formerly was so dangerous, is now done by machinery, and every precaution is taken to prevent the escape of the white lead dust. All of the rollers are kept in perfectly tight casings, and the whole apparatus is also enclosed by light partition walls. All the doors are double. We see, therefore, that in these fine works all precautions that hygiene may suggest have been taken.

Grinding white lead in water.—The white lead which has been dry powdered between the rollers, is sifted, and the fine portions fall into a closed cistern under ground, where they are wet with water.

The wet white lead is then ground under horizontal stones, twenty of which are in use. A soft paste is thus obtained, which is received in tubs, and these are carried by mechanical arrangements to the drying room. There the paste is put into porous conical pots, which are ranged upon shelves.

Drying rooms.—These rooms are heated during the winter by means of large cast iron stoves, burning bituminous coal. In summer a proper ventilation is sufficient to dry the white lead.

Mr. Lefèvre tried to light the drying rooms with the gas manufactured in the works, but he has been obliged to abandon the idea, since the sulphuretted hydrogen of the gas blackened the surface of the lumps of white lead, transforming it into lead sulphide. This inconvenience we think may be avoided by carrying off the gases of the combustion through a hood and pipe placed above the burners; or by using a gas containing but a very slight proportion of sulphuretted hydrogen.

The white lead in pots remains for ten to twelve days in ordinary drying rooms, and loses the greater part of its water. The lumps become consistent, and contract enough to be easily removed from their pots. Their desiccation is then completed upon the shelves of other drying rooms, heated at from 40° to 50° C., with hot air. The lumps which have preserved their shape are wrapped in blue paper; those which have been broken are powdered. The pots are cleaned with iron knives, and as the adhering white lead is still moist, this operation is considered to be quite devoid of danger.

Powdering lump white lead.—For several years the demand for lump white lead has been decreasing, and the greatest consumption is that of the powdered product.

By the old process, the lumps of white lead were pulverized under vertical stones running upon horizontal stone platforms, and the powder was then sifted. Notwithstanding the care and attention which were taken, there was always a very fine dust of white lead flying about the rooms, and the men were subject to lead colic.

Instead of vertical stones working in the open air, Mr. Lefèvre employs horizontal stones enclosed within a perfectly tight metallic drum. The lower stone does not move, but the upper one makes two hundred and seventy-six revolutions per minute.

On the top of the metallic drum there is a kind of coffee mill, which breaks the lumps of white lead before they pass between the stones. With four pairs of such stones (white marble), it is possible to powder every day, 31,000 kilogrammes of white lead.

The pulverized product is thrown off against the drum by centrifugal force, and falls into closed troughs by two diametrically opposite openings. The troughs deliver it into metallic revolving sieves, enclosed within a box with double doors. The sifted powder is received in a wagon holding about 1200 kilogrammes of substance, which is removed only when the dust has entirely subsided.

Since Mr. Besançon, in his works at Ivry near the gate of Fontainebleau (Paris), has established apparatus for grinding white lead in oil; the employment of this product has increased so rapidly, that this manufacturer sells seven-eighths of his white lead ground in oil.

Mr. Lefèvre has also established this preparation in his works. The powdered white lead is put with oil into an apparatus similar to a kneading machine, the blades of which thoroughly mix the substances. The paste obtained is then passed through three pairs of rollers, which laminate and finish it for the packing barrels.

Mr. Lefèvre also uses horizontal stones for grinding white lead in oil; five pairs of such stones are employed, besides the twenty other pairs for the grinding in water.

The men employed at grinding always wear gloves of lamb skin.

Packing white lead.—This operation is often a cause of lead colic. To prevent the production of dust, Mr. Lefèvre lets the white lead into the barrel slowly and carefully, and then compresses it by means of a screw, which pushes down a wooden block of a diameter slightly less than that of the barrel. A new addition of white lead is compressed in the same manner, and the operation is continued until the barrel is thoroughly filled.

The packing of the lump white lead is effected as follows: Rows of lumps, already wrapped in paper, are formed as close as possible; and when the barrel is half filled, it is shaken after it has been covered with several thicknesses of cloth. These are removed when the dust has subsided; but there is very little dust when the lumps are wrapped in paper. The packer has always two barrels on hand, so as not to lose time, and when one is filled, the cover is immediately put on.

All the rooms in Mr. Lefèvre's works are kept perfectly clean, and the clothing of the men is of such a nature as to prevent the contact of the white lead with the skin.

From what precedes, we see that MM. Lefèvre & Co. have taken all possible precautions for protecting their men from lead diseases, which are always dangerous and sometimes mortal. They have improved the operations of casting the lead, taking the beds apart, separating the white lead from the spirals, grinding the white lead in water or oil, filling and emptying the drying pots, dry grinding, and sifting and packing.

C. *Safe Apparatus of Mr. Ozouf.*

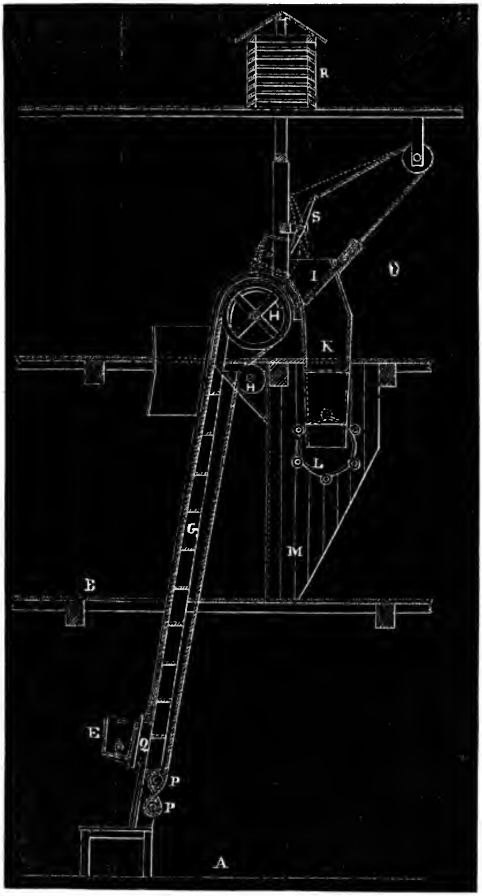
Mr. G. H. Ozouf, to whom we owe several ingenious apparatuses for the manufacture of gaseous waters, has invented, for the preparation of white lead by the Thénard process, an apparatus which rapidly combines the carbonic acid with the acetate of lead in a closed vessel, into which both are pumped by steam-power. Under pressure, the combination is said to be instantaneous, and there is produced a white lead of excellent qualtity, which needs but to be separated and dried. The description of this interesting apparatus is found in the *Technologiste*, vol. xxii. p. 519, year 1861.

D. *J. Poelmann's Machine for Separating the White Lead from the Metal.*

Mr. J. Poelmann, manufacturer of white lead, has also endeavored to render the operations less unhealthy by inventing a machine for separating the white lead from the non-corroded parts of the coils or buckles.

Figs. 33 and 34 represent two vertical sections of the apparatus. A is the ground-floor of the works, B that of the second story, and C that of the third. D, under the roof. E, box to hold the corroded lead before the white lead is separated. F, crank driving the gearing P P, which carries the box. G, wooden ladder with iron rails fixed upon, H H, pulleys, carrying the cord attached to the box E. K, trough delivering the material to the metallic sieve L. M, reservoir for the sifted white lead. Q, small car upon which the box E is fixed. R, latticed loft on the roof for ventilation. S, draw beam for opening the trap-door I of the trough K, when the box empties itself of its contents.

Fig. 33.

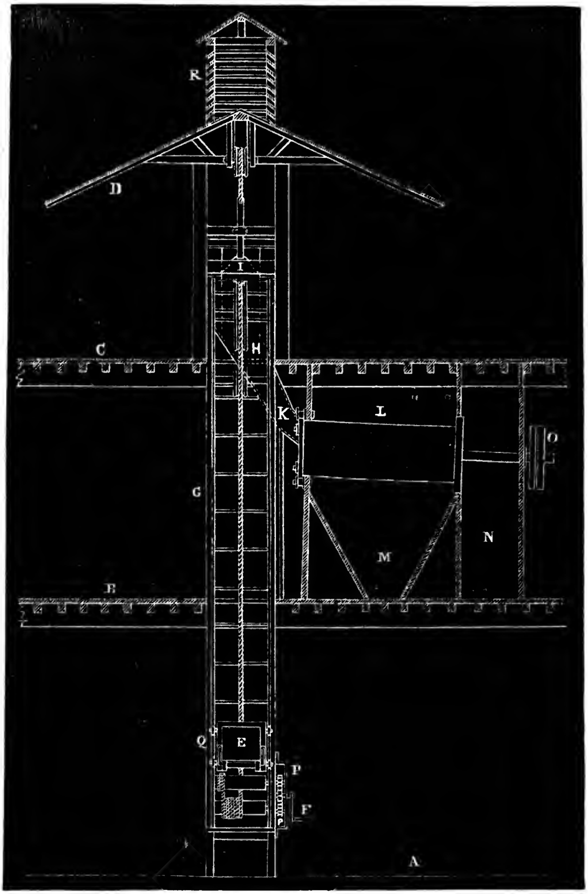


The metallic lead, separated from the white scales, is received into a separate box, tightly closed.

E. *Precautions taken to render the Manufacture of White Lead less unhealthy.*

In the examination made by the delegates of the Société d'Encouragement, of the manufacture of white lead at Portillon, near Tours, and which we have already described, the salubrity of the processes was

Fig 34.



especially considered. The conclusions of their report may be found interesting.

1. The works are well adapted for this manufacture, and the calcining furnaces, being built in the rock, preserve their heat.

2. All possible precautions have been taken for saving the men from the toxical action of the lead preparations.

3. The workshops are well ventilated, and supplied with railroads, hoists, and other labor-saving appliances.

4. The men are obliged to dress in a complete set of working clothes, which are furnished, washed, and kept in order at the expense of the administration. There are hot baths in the works.

5. A doctor, paid by the direction, gives the necessary medical care to the sick, and every week makes a general inspection at the works. Thus, a beginning of lead disease is prevented from becoming dangerous by suitable regimen.

6. Lastly, we consider that the manufacture of white lead at the works of MM. Lallu & Delaunay is as harmless as practicable, and that every precaution has been taken to prevent the contact of poisonous substances. Mechanical has been substituted for hand work wherever it has been possible; and where manual labor cannot be replaced there is no danger.

We have had the pleasure of seeing that a complete suit of working clothes was furnished by the direction to the men, and that they could not enter the workrooms without them. At the end of the day, and before getting their own clothes, the men have a thorough washing with soap and water. Besides all these precautions, *all the men* are examined every week by a doctor, who frequently orders medicated baths prepared in the works.

We have also seen with great satisfaction that the manufacture of white lead ground in oil is daily increasing at Portillon. When its employment shall become general, and no lump white lead is sold, we may rely on a termination being put to the diseases due to white lead.

§ 3. *White of basic chloride of lead.*

For some time past the effort has been made to replace white lead or carbonate of lead by a basic chloride of lead, which is much less soluble in water than the neutral chloride. Being uncrystalline, it possesses great body or covering power.

According to Mr. L. Brumlen, of New York, the lead is finely granulated by passing it through metallic sieves, and then put into three wooden tubs 1.50 metre in diameter and 0.60 deep, which are disposed so as to empty their contents one into the other by opening spigots placed near their bottoms. The top vessel is filled with vinegar (one litre of which saturates 350 grammes of carbonate of soda) or with a solution of neutral acetate of lead holding a little over 5 per cent. of it.

The lead which has been thus moistened becomes rapidly oxidized, and there is formed a neutral acetate of lead. By repeating the operation the basic acetate is obtained, and this will be the more readily produced if the solution already contains the neutral acetate. Up to this point the process does not present anything very new, since it is generally employed for preparing neutral acetates. The same person also states that litharge may just as well be dissolved in acetic acid.

The solution of acetate of lead is precipitated in the state of neutral chloride by hydrochloric acid—the clear liquid and the washings are used again as acetic acid. The neutral chloride of lead is then digested with basic acetate of lead until it has extracted sufficient lead from the latter to become basic. The clear liquor is decanted, and contains a neutral acetate of lead. The precipitate of basic chloride of lead is washed and dried.

The solution of neutral acetate of lead of the second operation is employed for the preparation of the basic acetate. Therefore, there is very little waste of acetic acid, which is the costly material.

§ 4. *White of sulphite of lead.*

Carbonate of lead is not the only salt of this metal which will furnish a white pigment, and several attempts have been made to substitute other salts for the carbonate.

Sulphite of lead is a white and insoluble powder, which possesses body and does not blacken by the contact of sulphuretted hydrogen. Mr. Scoffern, who has proposed its employment, says that it is obtained in the following manner: Sulphurous acid is prepared by heating sawdust with concentrated sulphuric acid, and the gas is passed through a solution of basic acetate of lead. There is formed a precipitate of sulphite of lead, and the liquor is a solution of neutral acetate which may be rendered basic by boiling it with litharge, as in the Thénard process

§ 5. *White of tungstate of lead.*

Large quantities of tungstate of soda are employed in English dye works as a mordant substitute for tin salts. 50 kilogrammes of tunstate of soda are dissolved in the smallest possible quantity of boiling water, and another hot and concentrated solution of acetate of lead is poured into the former as long as a precipitation takes place. After settling, the liquor is decanted, and the tungstate of lead is drained and washed. The liquors contain the soluble acetate of soda, but the basic salt of lead is transformed into the acid tungstate by a treatment with nitric acid (sp. gr. 1.3) or acetic acid (sp. gr. 1.05), diluted with their volume of water. The mixture is stirred now and then, and when the precipitate has acquired a certain consistency, the liquor is decanted, and the tungstate is washed with cold water. After draining upon cloth filters it is dried upon porous stones, which are heated at a moderate temperature in stove rooms. The decanted liquors or washings are saved on account of the oxide of lead they hold.

This process, as well as the two following, has been indicated by Mr. Spilsburg. The pigments obtained are costly, do not cover better than white lead, and are open to the same inconveniences.

§ 6. *Antimonite of lead.*

If we boil fifty parts of metallic antimony with twenty parts of concentrated sulphuric acid, sulphurous acid is disengaged, and there remains a white saline mass, which is a sulphate of antimony. This salt is heated until it no longer produces acid fumes, and is then transformed into antimonious acid by a calcination in a crucible with twenty-one parts of dry carbonate of soda. The fused substance is boiled in water, and the solution is decomposed by neutral acetate of lead. The precipitate is a heavy antimonite of lead, which is separated from the liquor holding acetate of soda. The pigment is collected upon filtering cloths, and when it has become pasty, it is formed into lumps which are dried upon bricks in a stove room, at the temperature of 60° C.

§ 7. *Antimoniate of lead.*

A mixture of one part of sulphide of antimony and five parts of nitrate of potassa, is deflagrated in a red-hot crucible, or upon the bed of a reverberatory furnace. The calcined product is almost entirely soluble in boiling water, and the solution is decomposed by another of neutral acetate of lead. The precipitate is separated, washed, and dried in a stove-room. This antimoniate, when pure, is white, heavy, and possesses a certain body.

§ 8. *Antimony whites.*

Many attempts have been made for employing the oxide of antimony in painting, but they seem to have met with but little success, although the antimony white possesses many good qualities. It stands water, is as opaque as white lead, is scarcely acted upon by sulphurous fumes or sulphuretted hydrogen, and it produces durable painting especially suitable for outside work.

1st. *Antimony White of MM. Bobierre, Ruolz, and Rousseau.*

It is intended by this process to substitute for white lead a substance which contains no lead, is not so dangerous to the health of workmen, and which may be obtained at a price equal or less than that of white lead.

After many experiments, these manufacturers gave the preference to the oxide of antimony, which may be prepared by known processes; nevertheless, they consider that the following method is more economical:—

"In an apparatus, which may be modified in many ways, a brick oven or a cast-iron furnace for instance, there are made to play on the heated surface of sulphide of antimony, a draft of air and a jet of steam which may be regulated for each kind of sulphide employed. All the sulphur escapes in the state of sulphurous acid, which may be saved, and the antimony is converted into the white oxide, which is collected in receivers placed at the end of the heating apparatus.

"This product may also be prepared in an ordinary roasting furnace, but it is not so comminuted as that obtained with the aid of steam. Oxide of zinc, other white oxides, and certain compounds prepared in a similar manner, acquire peculiar properties which were, until now, unknown.

"The product thus prepared may be ground immediately in oil, without passing through the operations of drying, pulverizing, sifting, etc.

"Considering the abundance and the cheapness of the natural sulphide of antimony, the white oxide may be obtained at a cheaper rate than white lead. Moreover, its covering power is at least twice that of the best white lead."

2d. *Antimony White of MM. Vallê and Barreswill.*

Here is the process of MM. Vallé and Barreswill, as explained by themselves:—

"We wish to record the results which we have obtained in our study of various chemical compounds, intended as substitutes for white lead in oil painting.

"Many experiments have already been made on this subject, and are found in the treatise on painting by Mr. de Montabert. It results from our own researches: 1st, that several lead compounds, other than the carbonate, may be used the same as white lead. 2d, that antimony, after lead and bismuth, is the metal which furnishes white pigments with the best covering power. This observation, mentioned by Mr. de Montabert, has since been pointed out anew by Mr de Ruolz (*Technologiste*, 5th year, page 155).

"The same as with white leads, the body or covering power of antimony whites varies with their mode of preparation.

"Mr. de Montabert states his preference for the oxide of antimony; ours is for Algaroth powder, which appears to us to possess properties similar to those of white lead. However, we reserve for ourselves the right of employing the oxide (prepared from the oxichloride and carbonate of soda) sublimed or not. Here is the mode of preparation of this new white:—

"The Algaroth powder is obtained by the treatment of the sulphide of antimony by hydrochloric acid. The sulphuretted hydrogen is made to burn, and the sulphurous acid produced is employed in lead chambers for the manufacture of sulphuric acid.

"The clear and settled chloride of antimony is decomposed by water.

"The hydrochloric acid resulting from this decomposition, and which still retains small proportions of antimony, is used for condensing hydrochloric acid gas, or for separating the gelatin from bones.

"We also manufacture the new antimony white by treating with hydrochloric acid, either the residue of antimony ore calcined at a low temperature, or the product of the action of sulphuric acid upon the sulphide of antimony.

"The sulphurous acid resulting from the treatment of the antimony ore is employed, either for the manufacture of sulphuric acid, or for that of sulphurous acid and sulphites ; in fact for all the uses of sulphurous acid.

"For the manufacture of antimony whites, Algaroth powder, and oxide by the dry or by the wet way, we make no difference whether the sulphide of antimony contains iron or not."

3d. *Antimony White of MM. Hallett and Stenhouse.*

MM. G. Hallett and J. Stenhouse employ a natural oxide of antimony, or an ore where the sulphide and the oxide are associated together. The mineral is finely pulverized, and separated from its gangue by washing and mechanical processes. The heavy metallic portions are calcined in a reverberatory furnace, and the sulphur is driven off as sulphurous acid. The residue is mostly antimonious acid, which, after being further powdered, is mixed with oil or varnish.

The product is often contaminated with small proportions of lead, copper, or iron, which diminish its whiteness. In such a case it is reserved for inferior painting.

The pure antimony white is less affected by sulphuretted hydrogen than white lead. It possesses more body than zinc white, but less than white lead.

§ 9. *Zinc white.*

For a century the unalterability of zinc white was known by chemists, and Courtois, of the Laboratory of Dijon, mentioned it in 1770 to the academy of that city. Three years later Guyton de Morveau published a memoir on the same subject, which was reprinted in the *Encyclopedie Méthodique des Arts et*

Métiers, then published. After several experiments, this learned chemist proved, in the presence of the Prince de Condé, that painting done with tartrate of lime, tin white, and *zinc white*, and exposed to the contact of sulphuretted hydrogen, was not changed in color.

In 1796, Mr. Atkinson, of Harrington, took out a patent for the application of zinc white, and Guyton de Morveau, in the *Annales des Arts et Manufactures*, claimed for France the priority of invention, since, in 1781, Courtois had begun the manufacture of zinc white on a large scale, and that stores existed at Paris and at Dijon for the sale of that material. Moreover, zinc white was already employed in France for artistic paintings, for mixing with other colors, etc.

The inside paintings of the man-of-war *le Languedoc* having been done with zinc white, in 1786, a commission for its examination made the following report:—

I. The painting with zinc white is handsome, but not so bright as that with white lead;

II. The smell of the fresh zinc paint is not so strong or disagreeable as that of white lead;

III. The zinc paint took six days to dry, whereas four days were sufficient for white lead;

IV. 250 grammes of zinc white and the same quantity of nut oil were sufficient to cover a surface of a little above 3.80 square metres, etc.

A copy of this report being transmitted to the Marshal de Castrie, then Secretary of the Navy, he recommended zinc paint for the insides of ships.

In a report made at the Institut, in 1808, by Fourcroy, Bertholet, and Vauquelin, we remark the following passage: "Among the products manufactured by Mr. Mollerat there is a *zinc white*, the use of which should be strongly recommended. Its defects are so slight in comparison with those of white lead, that it should be adopted, at least in house painting. Besides its salubrity, it gives purer colors; and, if its brightness is less at the beginning, it does not darken. With equal weights it covers a larger surface than carbonate of lead, and, although it is more dry under the brush, this is easily remedied by charging the brushes oftener, or giving another coat."

Lastly, in September, 1844, Mr. Mathieu sent to the Academy of Sciences a memoir on the *oxide of zinc*, in which he says that he obtains that product in a state of great purity, and by a much cheaper process than those then followed. Mr. Mathieu does not indicate the process, but he insists on the economy of the new method, and on the future of the oxide of zinc, which ought to take the place of white lead in the majority of cases. Moreover, it does not compromise the health of the men employed in its manufacture.

How is it then that, notwithstanding all these researches, successful trials, and honorable testimonials, the zinc white has not reached the place it ought to occupy in the arts?

A contractor in painting work at Paris, Mr. Leclaire, after acquiring a full knowledge of what had been done before him, has established at Courcelles, near the Seine, large works for the manufacture of zinc white, and has added several important improvements.

1st. *Manufacture of Zinc White, by Mr. Leclaire.*

Mr. Leclaire has established in his works a Silesian furnace with ten retorts. An arrangement of scrapers keeps the mouths of the retorts constantly open, and in front of them is a very small chamber, the floor of which is movable, and with a door which opens in the room where the furnace is. The top of this small chamber is connected with the upper part of the condensing rooms, which stand on the right and left of the furnace, and are deeper than the level of the furnace floor.

A powerful draft exists at the end of a series of cloth drums which receive the last particles of oxide of zinc. The floors of the condensing rooms are provided with hoppers, through which the oxide falls into the barrels.

Manufacture.—When the furnace is at the proper temperature, the door of the small chamber is opened, and the zinc is introduced into the retort. The door is then closed and luted, and the movable floor lifted. The combustion of the zinc begins immediately, and ceases only when all the metal is burned out, that is, oxidized by the oxygen of the air which comes through the lower part of the chamber. The oxide of zinc, according to its degree of lightness, is carried to a greater or less distance, and is collected in the hoppers placed at the bases of the different condensing apparatuses.

With two furnaces it is possible to produce every day 6000 kilogrammes of oxide of zinc, which is sold at from 70 to 75 francs per 100 kilogrammes.

There is no more difficulty in painting with zinc white than with white lead. Zinc white may be perfectly well mixed with oil, without grinding, by operating as follows: The zinc white, oil, and essence of turpentine are mixed together, and allowed to stand for about six minutes; the whole is then stirred with a brush and passed through a sieve.

Zinc white, whether alone or mixed with other pigments, is used for oil and water colors, for varnish, and for distemper painting, etc. Zinc white may also be used: I. In the manufacture of smooth papers and of visiting cards as a substitute for white lead; II. As a component part of mastics for keeping tight the joints of steam engines; III. For a face powder, colored with a small proportion of carmine; IV. And in the manufacture of Brussels laces.

Zinc white may be mixed with various pigments possessing durability, such as the oxides of iron, charcoal, oxide of manganese, ultramarine, etc. etc., and will then furnish colors, the tones of which will remain permanent, and this is a great advantage in painting.

The white or gray pigments prepared with the zinc oxide are not, like those with a basis of white lead, altered by hydrosulphuretted fumes. Repeated trials have been made which prove that painting with zinc oxide stands well in privies, and in those places where Barèges (sulphur) baths are administered.

An experiment has also demonstrated that zinc paints may be employed, like red lead and orange mineral, for preserving iron from oxidation.

Mr. Leclaire has indicated a method of preparing drying oil without lead, but with the peroxide of manganese. 200 parts of boiled linseed oil and 10 parts of peroxide of manganese are boiled together for six and eight hours, and the mixture is frequently stirred. After cooling and filtration, the oil has become a good dryer.

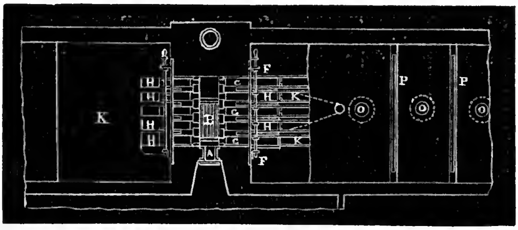
Lastly, Mr. Leclaire has also prepared variously colored pigments, with zinc as a basis, for artists and house painters. These pigments are:—

1. *Gold button (bouton d'or) yellow*; 2. *Lemon yellow*; 3. *Pale yellow*; 4. *Baryta yellow*; 5. *Dark English green*; 6. *Light English green*; 7. *Milori green*; 8. *Green earth.*

We find in the *Technologiste* the following description of a process for the manufacture of the oxide of zinc:—

Zinc white may be prepared by the distillation of the zinc ore or of the metal in special furnaces.

Fig. 35.



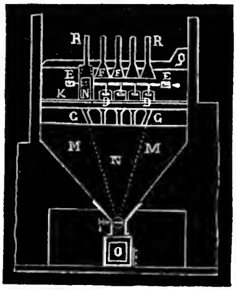
Description of the apparatus.—Fig. 35 is a horizontal section of a glass furnace, with certain modifications which will be explained further on, and with the additional fixtures necessary for the manufacture and the condensation of zinc white.

Fig. 36 is a transverse section of the furnace.

Fig. 37 is a longitudinal section.

A, door of the furnace. B, fireplace. C C, retorts made of clay or of any other substance able to stand a high temperature. There are five retorts on each side, but the

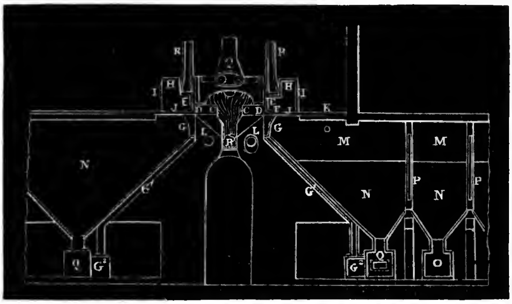
Fig. 36.



number may vary. D D, openings of the retorts, through which the products of the distillation escape. F F, iron rods or scrapers for keeping the mouths of the retorts open. E E, horizontal bar to which the scrapers are attached. By pushing it backwards and forwards, the scrapers do their work. Motion is imparted by hand or by power. G G, hoppers which receive the heavy portions of the calcined zinc. They are placed below the mouths of the retorts, and their lower parts are connected by short pipes with a general trough G^1, which delivers the products into the receiver G^2.

It is well understood that these hoppers receive only the heavy portions of the distilled products, or the scrapings from the mouths of the retorts, the weight of which is too considerable to be carried by the draft into the oxidizing chamber.

Fig. 37.



H is a small iron cage which isolates each retort from the others, and which stands upon a low wall. It may be moved or shifted by means of a crane or of rollers. The open part of these cages is in front of the mouths of the retorts, so that the distilled products may pass from the cage into the oxidizing chambers and condensers. In Fig. 35 some of these cages are represented, the others are not. Their back part may be opened or closed, as desired. J is an opening on the floor K, which is closed with a hinged trap door, raised or lowered by means of a chain I, one end of which passes through the partition, so as to operate without opening the cage. Other ways of moving this trap door may be devised.

The arrangements H, I, J could be adapted to the furnaces where zinc is smelted. There is always a certain proportion of zinc oxide formed which is lost, and which could be saved in the above-described manner, or by closing with a cloth the space where the zinc is collected. If the iron cage or chamber be used, a small opening is made on the partition I, which is closed with a glass, so as to allow of the watching of the distillation. The same result will be obtained by fixing iron plates on each side of the opening of the retorts. Another movable plate will be used as a cover.

K, floor carrying the cages H, and separating this part of the apparatus from the oxidizing chamber. The air drafts may be introduced into the chamber having K for the floor, or through the floor itself, which, then, should be hollow. Fresh air is necessary, in order to lower the temperature of the chamber above the floor.

L, hot air pipe communicating with the hoppers G G, and carrying away the white oxide into the oxidizing chamber. Instead of hot air, cold air may be passed through the cages H, or, if it be thought desirable, a mixture of cold and hot air may be introduced.

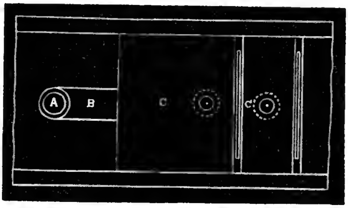
M, oxidizing room, where the metallic vapors are oxidized by atmospheric air, as soon as they escape from the retorts. N, portion of the oxidizing chamber, where there are cloths for sifting the products. The lower part is hopper shaped, and conducts the oxide of zinc into receivers below. There are valves, registers, etc., for letting the product in or out.

The whole of the product may be collected without loss, by means of properly arranged vessels or receivers filled with water, and provided with two tubes. One of the latter communicates with the oxidizing room, and dips, at the other end, into the water of the receiver. It conducts the zinc white from the oxidizing room into the receiver. The end of the other tube does not dip into water, but takes in the air of the receiver and produces a vacuum in the other tube, thus forcing the descent of the products. O, O are the receivers for the oxide. P, P, partitions of metallic wire, or cloth, for allowing the air to pass through, and for sifting and retaining the products. Q, exhaust tube for moving the air through the sifting surfaces, and attracting the products towards the receivers.

R is another tube or hood placed on top of the opening of each retort, and intended for the escape of the volatilized products, when the charge is put in, and when the communication with the oxidizing room is closed by the trap-door J. The hood R carries the volatilized products, by suitable conducts not seen in the figure, into the oxidizing room, or into a special condensing apparatus. A draft may be produced, either by heating the hood, or by an exhauster. This hood is closed during the distillation, as long as the metallic vapors pass directly into the oxidizing chamber. In this case, the vacuum or exhaust is produced by the lost heat of the furnace.

In the preceding arrangement, the retorts are separated each from the other, and we readily understand that this result may be arrived at by other analogous methods. For instance, the floor K may be disposed so as to be raised or lowered at will, in order to separate the retorts one from another. It may be divided into as many sections as there are retorts, so that, by raising or lowering one of them, the communication with the oxidizing room may be established or closed.

Fig. 38.



The retorts may also be separated by partitions and rendered independent of each other. The hood R may have such dimensions and exhausting power as to carry all of the products into the condensing rooms.

Fig. 39.

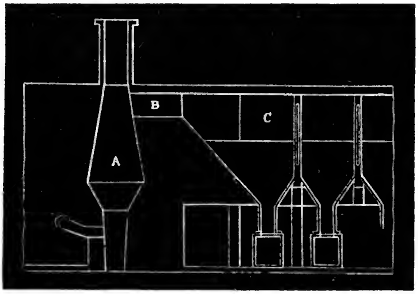


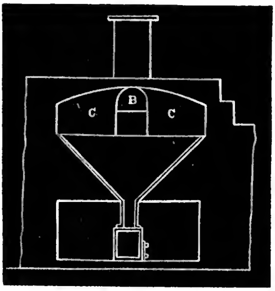
Fig. 38 represents a horizontal section of another furnace for the manufacture of zinc white.

Fig. 39 is a longitudinal section.

Fig. 40 is a transverse section.

This furnace is closed on top, either by a cover which may be moved for charging the retorts, or by a hopper filled with the substances for the operation. It could be hermetically closed on top, and opened on the sides for charging. Lastly, the materials may be introduced through the opening B, and in this case, an inclined plane is so disposed as to receive the materials.

Fig. 40.



All these dispositions, and others, are well known, and we shall only examine the principal details.

A, air furnace of proper size. B, opening through which the products pass into the oxidizing room C, which is arranged as in the preceding figures. Between the various hoppers of the oxidizing room, there are metallic or cloth sieves, to arrest the heavier products or the impurities carried away through B. The oxide of zinc, being very light and comminuted, passes through these screens. The opening B may be provided with a register or damper, for closing the communication between the furnace and the oxidizing rooms, whenever the circumstances require it.

The charging hole may be provided with a hopper, or any other apparatus for delivering the materials as the distillation progresses. Besides the current of air caused by the draft or blast, and necessary for the combustion, another injection of air could be made to furnish the necessary oxygen to the vapors of zinc, either in the furnace or in the flue B.

The furnace may be circular in shape, or horizontal, or more or less inclined. Instead of one opening B, several may be made at different heights, even near the fireplace; in which case the products, as soon as formed, are carried directly into the oxidization room, without being obliged to pass through the materials piled above. A reverberatory furnace may be employed, and also a coke-oven; but in the latter case, there should be a fireplace heating the furnace by means of flues circulating under the hearth or sole, and in the side walls. A top opening will be used for charging, and a side one for the passage of the products into the oxidizing and condensing rooms.

Fig. 41.

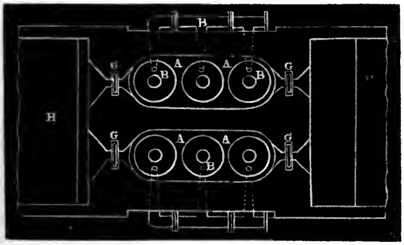


Fig. 42.

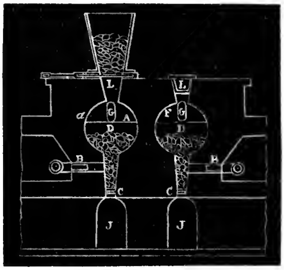


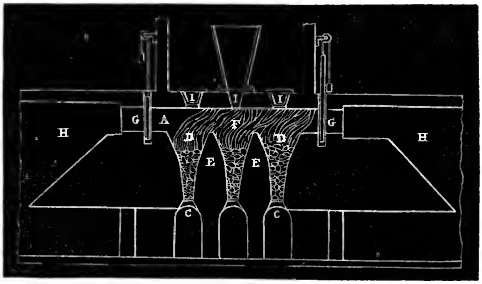
Fig. 41 is a horizontal view of another kind of furnace for the manufacture of oxide of zinc.

Fig. 42 is a transverse section.

Fig. 43 is a longitudinal section.

We see that this furnace consists of two horizontal and parallel flues or retorts, with fireplaces receiving a blast of air. A A, flues built of fire bricks. B B, tuyeres for hot or cold air blast. C, lower part of the fireplace, where the cinders and ashes are collected. These are removed now and then through a lower opening. But if large ash pits J J are left in the brickwork, the part C is closed with a grate or damper. With grate bars sufficiently close to retain the ore, and large enough to let the cinders fall through, a natural draft of air may be substituted for the artificial blast. In this case, the proper fluxes should be added to the ore, for transforming the earthy parts into fluid cinders.

Fig. 43.



D D are fireplaces opening into the same arched flue F. The charge of ore and coke is piled up to the level *a*. E E, brickwork separating the fireplaces.

The air may be admitted into the flue F, either by compression or exhaustion, for oxidizing the metallic vapors and carrying them into the condensing rooms. At each end of the flue F, there are dampers G G, establishing the communication with the condensing or collecting rooms. H H are these rooms, which are arranged in the manner previously described. Instead of two rooms only one may be used, if desired. I I I are the openings for charging, which stand immediately above the fireplaces. They are closed by a tight cover, or by a metallic hopper filled with the ore mixture, which is thus dried.

We readily see that this apparatus may be modified in several ways. For instance, instead of two series of tuyeres, only one, or a greater number, may be employed. The number and the sizes of the fireplaces may vary. The brickwork may be raised still higher, and less space left for the passage of the air and the metallic vapors. The two collecting chambers may be replaced by one. These modifications do not change the principle of the invention, which consists in a horizontal tubular flue, connected with one or several fireplaces using a natural or forced draft of air, and which communicates with rooms into which the products of the combustion are driven by exhaustion or by compressed air.

Mode of operation.—1. *With the retorts.*—Ingots of zinc are charged into the retorts, which have been previously brought to a white heat. As soon as the whole charge is in, the iron cage H is closed, and the trap-door on the floor is lifted, so as to put the retort into direct communication with the oxidizing room. The vapors of the distilled zinc become oxidized by the air, and the white oxide is constantly drawn into the receiving or condensing room by the vacuum maintained in the pipe R. The oxide is arrested by metallic screens which allow of the passage of the air, and falls into hoppers, which deliver it into the receivers. When the retort is empty, the trap-door is closed, the damper over the hood is lifted, and a new charge is put in, and the operation continues as before.

If we operate with a zinc ore, or an oxide of this metal, it is mixed with half its weight of charcoal, coke, or bituminous coal, as is done in the ordinary treatment of zinc ores.

If the ore is a blende, that is, a sulphuret, it is necessary to add a certain proportion of peroxide of manganese, carbonate of lime, or oxide of iron, in the ratio of the sulphur contained in the ore.

2. *Air furnace.*—When we employ the air furnace, the charge of ore is mixed with the above-mentioned substances, and with a certain proportion of a proper flux. As soon as the zinc becomes separated from the foreign substances with which it was combined, its vapors are rapidly oxidized, and the zinc white is collected in the rooms already mentioned.

3. *Reverberatory furnace or coke oven.*—The working of the reverberatory furnace is so well known, that it is useless to describe it here. The mode of charging and cleaning it is the same as with other ores. This method, however, does not appear so advantageous as the others. When furnaces, similar to coke ovens, are employed, they are charged while very hot with metallic zinc or its oxides, alone or mixed with coal. A current of air passes, either through the furnace, or only at the opening through which the metallic vapors escape to go into the collecting room. If the metal be employed with this apparatus, or any similar one, it may be made to fall by drops by passing it in the molten state through a metallic sieve.

4. *Horizontal tubular furnace.*—After the furnace has been brought up to the proper temperature with bituminous coal or coke, the mixture of ore and fuel is thrown in through the openings I I I, with a certain proportion of aluminous or calcareous flux to suit the nature of the gangue. The space F is left open. When blende is used without previous calcination, the ore is mixed with peroxide of manganese, carbonate of lime, or oxide of iron, in proportion to the sulphur held by the blende. The ore is decomposed,

and the metallic vapors are oxidized and collected in the manner previously explained.

Immediately after charging, and until the mass is in an incandescent state, gases and solid but light substances are disengaged, which, if received in the collecting rooms, would impair the whiteness of the products. This is the reason why two condensing rooms are employed, one on each side. One of these rooms receives the products distilled before the whole mass is in the incandescent state, and the other, by a change of dampers, is employed for the pure products. The disposition of the collecting or condensing rooms is common to all the various processes.

Fig. 44.

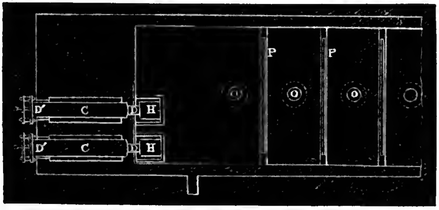


Fig. 45.

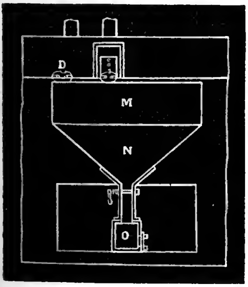
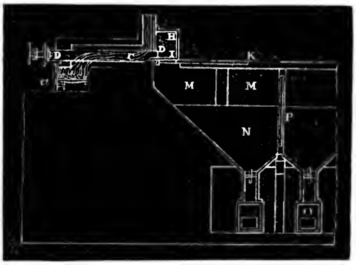


Fig. 46.



Figs. 44, 45, and 46 represent a furnace built in the manner of those employed in the manufacture of gas, but possessing the fixtures necessary to the distillation of zinc, the oxidization of its vapors, and the collection of the oxide.

Any number of such furnaces could be disposed one near the other, each having several retorts. The same letters in these figures correspond with similar parts in the preceding cuts; therefore, it is useless to explain them anew. The only difference is, that the retorts may be charged from the same room in which the fireplace is. The retort is open at both ends D, D′, the latter being that used for charging. During the distillation, this opening is kept hermetically closed.

With this disposition it is possible to dispense with the chamber or cage H, and with the floor K. Nevertheless, this apparatus is not so advantageous as others, and should be employed only in case of necessity.

2d. *Mode of Fabrication by Murdoch.*

A method of manufacturing the oxide of zinc, several years older than that previously described, has been indicated by Mr. Murdoch. Although there is a great analogy in the chemical processes, we shall mention it here, in order to complete the data relating to the oxidization of zinc.

By the ordinary methods of preparing the oxide of zinc, air is allowed to enter the retorts or vases holding the metal, and oxidizes the metallic vapors. Part of the oxide is collected in pipes adapted to the retort, but the greater portion remains in the retort mixed with impurities.

The improvement consists: 1st, In preventing the access of the air to the molten zinc or to the zinc furnishing materials held in the retort, and in burning the metallic vapors on the outside of that vessel in which they have been generated; 2d, In passing the mixture of air and oxide through sieves or screens, which retain the oxide; 3d, In producing a strong air blast or draft (by a blowing machine or otherwise) which is passed through the rooms where the oxide is produced and collected. The operation is thus assisted considerably.

For the manufacture of zinc oxide by this process, five rooms are employed: the retort room, the air room, the oxidizing room, that for the collection, and lastly, the inspection room.

The first of these rooms contains the furnace of the retort or generating vessel; and it is there that the operations of charging and cleaning take place. The retort which receives the zinc or its ore is of clay, and will stand a white heat. It has two openings, one of which is for charging and cleaning, and is kept hermetically closed during the distillation; the other is the outlet through which the metallic vapors escape into the oxidizing room.

The air room communicates with the outside atmosphere, and is provided with metallic or cloth screens which allow of the passage of the air, but prevent that of the floating dust. The air is therefore in a measure purified.

One of the extremities of the retort penetrates on to one side of the oxidizing room, and, as soon as the metallic vapors appear, they burn in contact with the air which comes from the air room. The white fumes or flakes resulting from this combustion and which are oxide of zinc, or *flowers of zinc*, are carried by the draft into the collecting room. A flue or trough connects the latter room with the stack of the furnace and thus creates the draft. Several screens of cloth or metallic gauze are placed before the opening of the air trough, so as to retain the oxide of zinc. These screens are now and then, or constantly, shaken, in order to separate the adhering oxide which, otherwise, would obstruct the passage of the air.

The inspection room is on the opposite side of the entrance of the retort in the oxidizing room. The partition wall has two openings: one with a colored glass to diminish the glare of the burning metal, and to allow of the watching of the operation; the other with a small door for passing and using a scraper, should the opening of the retort become obstructed.

3d. *Manufacture of Zinc White at Portillon, near Tours.*

The owners of the white lead works at Portillon have also established, at the same place, the manufacture of zinc white with a furnace holding seven retorts. The oxide of zinc, of which about 2000 kilogrammes are produced every day, goes upwards after its formation, and is collected in a series of cloth cylinders, delivering it into barrels through their lower extremities, which are easily closed and opened. There cannot be a loss of oxide, since the air draft has to pass through 600 metres of collecting space before it escapes into the atmosphere. The zinc white is ground in oil by processes similar to those employed, and already described, for the grinding of white lead at the same works. The oxide of zinc is put wet into the kneading machine, but the oil separates the water when the paste is passed through the grinding cylinders.

4th. *Snow White, Zinc White, Hopper White.*

The oxide of zinc, obtained by the combustion of the metallic vapors in atmospheric air, is not homogeneous. About one-half of the product is exceedingly light, and is called *snow white;* the remainder is more dense, and goes under the name of *zinc white.* Painters affirm that the latter possesses greater body or covering power than the former. Therefore, several manufacturers have tried whether it would not be possible to produce the dense quality without admixture of snow white. The thorough separation of the two oxides is not considered practicable. Mr. Bouquette's process consists in arranging and regulating the drafts of air in such a manner, near the outlets of the retorts, that the light snow white is carried upwards into a room above the furnace, whereas the heavy white falls into a hopper underneath the distilling vessels. The operation is not very regular.

We should remark that the zinc white collected at the beginning of the condensing apparatus, near the furnace, is a mixture of oxide of zinc with metallic zinc, and a greater or less proportion of cadmium, iron, and copper. The oxide from the tail end of the condensing rooms is always lighter, and the two kinds are generally mixed together.

Mr. Sorel thus describes a process for separating them: "A certain quantity of zinc, put into large muffles, is heated only to the point of fusion, and is then inflamed. The burning will soon cease if care be not taken to constantly rake off the oxide formed on the molten surface. The zinc, which is all the time in contact with the oxygen of the air, produces a very light oxide, which is carried away by the draft into the collecting rooms above the furnace. The oxide remaining on the surface of the bath is generally contaminated with other metallic oxides, and is made to fall into a receiver or hopper near the furnace. It bears the name of *hopper white*, and is not so white as that which has been volatilized. The advantage of this process is simply the separation of the two oxides.

"Hopper white covers more than snow white, but it is not so bright. In order to impart greater density to snow white it has been suggested to calcine it in clay crucibles, or, better still, to make it into a paste with water, and to form lumps which are dried in a stove room. The white, after these operations, is more difficult to grind, but it covers more and has a better appearance."

5th. *Saint-Cyr White.*

Another product, manufactured at the works of Portillon, and called *Saint-Cyr white*, is a mixture of white lead and zinc white.

6th. *Vitry White.*

This is a mixture in variable proportions of zinc white with sulphate of baryta. It is now seldom met with in the trade under that name, and, if sold as zinc white, constitutes a fraud which should be punished.

7th. *Various Pigments obtained with Zinc White.*

Zinc white is also employed as a basis of various pigments employed in painting. 100 parts in weight of zinc white and—

1	part of	indigo	= azure-white.
1	"	charcoal	= pearl-gray.
100	"	gray zinc oxide	= slate-gray.
2.5	"	chromate of zinc or lead	= straw-yellow.
6	"	yellow ochre	= stone color.
3	"	yellow ochre	= chamois.
3	"	vermilion	
10	"	sienna earth	= dark chamois.
2.5	"	chrome yellow	= lemon.
2.5	"	Prussian blue	
10	"	chrome yellow	= gold-yellow.
0.9	"	Prussian blue	= tint of azure-blue.
0.2	"	madder lake	
8	"	Prussian blue	= water-green.
100	"	chrome yellow	= grass-green.
8	"	Prussian blue	
50	"	yellow ochre	= olive-green.
12	"	black	
400	"	chrome yellow	= bronze-green.
6	"	Prussian blue	
6	"	black	

For obtaining pure or mixed hues, the following substances are also employed: Ultramarine, cobalt blue, Prussian red, ivory, bone and lamp blacks, oxide of manganese, etc.

8th. *Various Processes for the Manufacture of Zinc White.*

Many processes and apparatuses have been described and proposed for the manufacture of zinc white. They are generally based upon the oxidation of zinc vapors by the oxygen of the air. Some replace the retorts by muffles, or heat the zinc directly upon the hearth of the furnace, others employ a pot of fire clay. Certain manufacturers use a draft of pure air; others claim that the gases of the combustion of coke or charcoal, which have been passed and purified through lime, give a better oxidized zinc white. In countries where rich zinc ores are found, zinc white is advantageously prepared by the reduction of the ore with charcoal.

The great quantities of sulphate of zinc produced in galvanic batteries, are now without use. All its component parts may be utilized in the following manner. By a calcination in a clay vessel, the sulphate of zinc, when pure, is transformed into a white and light oxide for painting, and into sulphurous acid which may be dissolved in water, or used for the manufacture of sulphites, which are now employed in large quantities. Pure oxygen is also formed.

All these processes, conducted with the proper care, may furnish a zinc white of good quality. But we do not feel that we should fill up this manual with more extended explanations of methods, which, after all, do not appear superior to those which are well known and tried.

We should add that metallic zinc necessarily increases in weight, by combining with the oxygen of the air, and that one hundred parts of metal should give about one hundred and twenty-four of oxide. But in practice, the result is only from one hundred and ten to one hundred and twelve parts of white, on account of the loss occasioned by the impurities of the metal, and the waste of oxide carried away in the air, and escaping through cracks in the apparatus.

9th. *Uses of Zinc White, and Dryers.*

Zinc white mixes readily with all the liquids employed for white lead, such as oil and essence of turpentine; and as it is always in an impalpable powder, it does not need a protracted grinding to acquire the proper consistency. Glue size may also be employed.

The advantages of zinc white are, that it is scarcely poisonous; that it does not change the colors with which it is mixed, and that it does not darken by the fumes emitted by sulphuretted hydrogen or animal substances. On the other hand, it is slow drying, and dryers are necessary.

We have already seen, that in 1845, Mr. Leclaire had employed the peroxide of manganese for the quick drying of the zinc white. Here is the instruction published by the Society of the Vieille-Montagne, in a manual for the painters with zinc white:—

"The peroxide of manganese is broken into pieces of the size of peas, and after sifting the smaller particles, the remainder is thoroughly dried upon a piece of sheet-iron, but without being calcined. It is then wrapped in a piece of strong cloth, which is afterwards placed in a small basket of wire gauze with very narrow meshes.

"Well clarified linseed oil is poured into a kettle, which is held upon an iron plate above the fireplace, and the basket of peroxide of manganese is suspended in it from an iron rod crossing the kettle.

"The oil is brought to a temperature a little below the point of ebullition, and maintained there. Too much heat will cause the oil to boil over, and there is then great danger of fire. The heating should last twenty-four hours for large quantities of oil.

"The operation is completed and successful, when the oil has acquired a reddish tinge. It is then left to cool, is filtered, and packed in glass or stoneware bottles, which are carefully closed.

"The same manganese may be used any number of times; indeed it is better when it has already been employed. Before using it again, it is coarsely broken in a mortar and new manganese added; the whole is then sifted, and the proportion is fifteen parts of the mixture to one hundred parts (in weight) of oil.

"The first time manganese is used, it is put into the oil only on the second day of the heating, because fresh oils hold a little water, and the new manganese might act too powerfully and cause the inflammation of the liquid.

"If the manganese has already been used, it is put into the oil on the first day, before lighting the fire. Less heating is needed with fresh than with old manganese. In either case, the fire is urged but moderately, and the basket of manganese must be entirely covered with oil, without touching the sides of the kettle.

"If the dryer be too thick from a strong heating, essence of turpentine may be added to it when it is nearly cold, otherwise there is danger of inflammation. The proportion of the essence should be sufficient to reduce the dryer to the proper consistency for using and keeping it."

In his *Chimie des Couleurs*, Mr. J. Lefort makes the following observations on dryers:—

"In order to render dryers suitable for every kind of painting, and to facilitate their transportation, it has been proposed to mix them with slaked caustic lime. But as the latter contains an excess of water, it is heated at a moderate temperature in a draft of hot air, until the powder feels dry. The combination is a real drying calcareous soap, which being ground with colors and ordinary linseed oil, is a good substitute for drying oil. From four to six parts of drying soap in powder, are sufficient for one hundred parts of oil.

"Peroxide of manganese, especially when powdered, communicates to the oil a reddish tinge which is disagreeable for fine white painting. Of late years, this inconvenience has been remedied by the use of white salts of manganese; and experience proves that the majority of soluble salts of protoxide of manganese and zinc (sulphates, chlorides, acetates), when ground with ordinary linseed oil and zinc white, impart to the latter the drying property it was deficient in.

"It is absolutely necessary that these various salts should be entirely deprived of their combined water. Therefore, they are thoroughly dried upon plates heated at from 80° to 100° C., until they are perfectly white and opaque. They are then mixed in equal proportions, and finely powdered.

"These dryers which have been patented, and which are constantly employed in painting with zinc, are composed of sulphate of zinc and acetate of manganese, or of sulphate of manganese and acetate of zinc. Three or four parts are sufficient with the proper quantity of ordinary linseed oil, for one hundred parts of zinc white."

Moreover, we shall examine anew, in a subsequent chapter, the various dryers and compositions which have been proposed.

10th. *Adulteration of Zinc White.*

Zinc white is adulterated with sulphate of baryta and sulphate of lime.

The first adulteration is recognized by dissolving the oxide of zinc in diluted nitric acid, when the sulphate of baryta remains as an insoluble residuum.

The separation of the sulphate of lime is more difficult. The adulteration is generally made with a perfectly white sulphate of lime, in impalpable powder, which is sometimes called *atomic sulphate.* The suspected sample of zinc white is dissolved, with the aid of heat, in a small quantity of concentrated nitric acid. The solution is diluted with five or six times its weight of distilled water, then saturated with ammonia, and a few drops of oxalate of ammonia poured in. The precipitate of oxalate of lime is collected upon a filter, calcined, and transformed into carbonate which is weighed. A solution of chloride of barium, poured into the filtered liquor, produces a sulphate of baryta which is insoluble in water and in concentrated acids.

If the sample be already ground in oil, 10 grammes of it are calcined in a porcelain crucible, and when all the oil is decomposed, the cold residuum is treated by distilled water. A few drops of nitric or sulphuric acid poured into the liquor, will disengage sulphuretted hydrogen in greater proportion as the sample is more adulterated.

If the oil has been rendered drying by compositions of lime and sulphate of zinc, these substances should be determined by analysis, and taken into account in the search for the adulteration of the sample.

11th. *Danger and Salubrity of Zinc White.*

When this pigment began to be largely used in painting, its salubrity was considerably discussed. Some persons pretended that it was as dangerous as white lead; others, on the contrary, that it was entirely innocuous. Facts were brought forward by each party; but, without burdening this volume with all the documents on the question, it is certain that zinc white is not so dangerous as white lead to the health of either the workmen or that of the consumers. Nevertheless, it is not entirely innocuous, and, in certain cases, it has produced slight sickness, which may be avoided by care in its manipulation.

12th. *Use of Blende as a Substitute for White Lead and Zinc White.*

Blende, or sulphide of zinc, in the opinion of Mr. de Certeau, may be advantageously and cheaply substituted for white lead or zinc white in all the colors for painting. Its impalpable powder ground in drying oils, with or without essence of turpentine, will cover at least as well as white lead and zinc white, and the coats flow more easily under the brush. This color is very fast and durable, and does not change the other pigments with which it is mixed.

The only disadvantage of blende is that it is always more or less colored. The inconvenience is slight with those blendes which are colored a honey-yellow, and which are rightly considered the purest. That variety, when finely comminuted, gives a grayish-white powder with a yellow tinge, which may be employed for light colors in house painting. Mixed with 1 per cent. of artificial ultramarine, it produces a gray coat, slightly greenish. If, instead of blue, a small proportion of vermilion or ochre be added, the color is pinkish. With chrome yellow and a little red, we obtain a chamois. A pearl-gray is obtained by increasing the whiteness of the blende with ten or twenty per cent. of zinc white, and adding 1 per cent. of black.

Brown or reddish blendes cannot be employed in the preparation of light colors, such as those we have just mentioned; but they may be successfully used for dark colors, such as brown, black, maroon, olive-green, mahogany, etc.

There is no advantage in using roasted blendes, instead of the natural ones; because, by roasting, blende loses about one-sixth of its weight, generally becomes darker, and covers less. However, as roasting changes the color of the substance sensibly, it is an easy process of obtaining certain tones and hues, which could not be produced so cheaply in another way. Therefore, roasted blende may, by its mixture with the natural one, add new tones and hues to the colors resulting from this material.

Powdered blende is far from being as dangerous as white lead. Therefore, in the opinion of Mr. de Certeau, that substance possesses the advantage of popularizing the use of oil paints as well by a great reduction in prices, as by diminishing the use of a dangerous substance (white lead).

§ 10. *Baryta whites.*

1st. *Natural Sulphate of Baryta.*

The sulphate of Baryta, or Barytes, heavy spar, Barytine, Baroselenite, hepatite, stinking stone, Bologna stone, etc., is a white or reddish substance, very dense, which is found in the natural state forming veins with the ores of lead, silver, mercury, etc., and in many other rocks. It contains 34.37 parts of sulphuric acid and 65.63 parts of baryta.

Heavy spar is employed in the manufacture of a handsome white color, entirely innocuous, fast and resisting most reagents, but with little body or covering power. This white, fixed with glue size, is largely employed in the manufacture of paper hangings. It is also used for adulterating white lead and zinc white. We have previously said, that, in Germany, it was customary to add to it white lead for the preparation of Venice and Hamburg whites. In Austria, the pure sulphate of baryta is still sold under the incorrect name of Tyrolese white lead.

In preparing the sulphate of baryta for the arts, the whitest lumps of native ore are picked out, and coarsely broken, and charged into reverberatory furnaces. The heat applied is solely intended for disintegrating the substance, and arriving at a finer degree of pulverization. The grinding is done dry, and the fine resulting powder is thrown into large tanks filled with water. By stirring, and then letting it stand a little while, the heavier and coarser particles fall to the bottom. The water above, which has the appearance of milk, is decanted into settling basins, where the lighter suspended material has time to deposit. After another decantation of the clear liquor, the pasty white is collected, and dried in the air or in a stove room. It is then a very bright and dense white.

2d. *Artificial Sulphate of Baryta, Blanc Fixe.*

For several years we have found in the market, under the name of *blanc fixe* (fast white), an artificial sulphate of baryta, which is much better than the native sulphate. We owe it principally to Mr. F. Kuhlmann, of Lille, one of the greatest manufacturing chemists of France. Mr. Kuhlmann, in a memoir, read before the Academy of Sciences, has described the mode of preparation and the properties of this product, and we cannot do better than to present an extract from that memoir, which we do as follows:—

"In order to produce the artificial sulphate of baryta at a moderate price, I have endeavored first to reduce the cost of the acids which constitute the main expense of its manufacture. I have, therefore, tried more completely to condense the acid vapors, part of which are lost in our soda works to the prejudice of the manufacturers, of the public health, and of vegetation.

"By putting the natural carbonate of baryta (witherite), large deposits of which are to be found in the north of England, in contact with the vapors escaping from the salt decomposing furnaces or from the lead chambers, I have succeeded in saving a large proportion of the uncondensed vapors which no longer incommode the neighborhood or injure vegetation.

"In my works the baryta, dissolved by the condensed acids, is converted into the artificial sulphate by an addition of sulphuric acid. The recovered nitric and hydrochloric acids return to take part in a new operation, and increase the yield. I thus realize the double advantage to which my experiments have tended.

"But there is a loss of hydrochloric acid much greater than that resulting from imperfect condensing apparatus, *i. e.*, that resulting from the manufacture of chlorine or bleaching powder, which consumes the greater proportion of the acid.

"There is no chemist who has not deplored the fact, that more than one-half of the hydrochloric acid used, is lost in the state of chloride of manganese. This loss, in practice, amounts to two-thirds, on account of the impurities in the oxide of manganese. Its magnitude may be made apparent in considering that the manufacture of artificial soda, in France, consumes per year over sixty millions of kilogrammes of common salt. I think that I am below the reality in saying that the indicated loss amounts to two millions of francs per year, in France alone.

"That great loss has caused many to make search as to whether the residue of the manufacture of chlorine could not be made available and valuable. Notwithstanding many trials, the new uses have been few, and absorbing but a small proportion of the waste materials. This chloride of manganese has been applied to the purification of gas light, to the production of ammoniacal salts, and to disinfecting cesspools. In the large works of Mr. Tennant, near Glasgow, experiments have been made to regenerate the oxide of manganese, so as to use it again in the manufacture of chlorine. All their uses amount to little as regards the enormous quantity of residue. In the majority of cases, the price at which the chloride of manganese is sold is scarcely sufficient to cover the expense of concentration or calcination.

"Therefore, the liquid residue of the manufacture of chlorine has generally remained a cause of embarrassment to chemical works, and even of danger to general salubrity, whether it was let into running waters or lost in the ground through absorbing wells.

"After having condensed the acids lost in the air, all my efforts have tended to the saving of those held in the liquid residue.

"I have had the satisfaction of succeeding completely by using a reaction analogous to that by which Leblanc gave to France the manufacture of artificial soda.

"In the Leblanc process, a mixture in proper proportions of sulphate of soda, chalk, and coal, is transformed, at a high temperature, into insoluble oxysulphide of calcium and soluble carbonate of soda.

"In my process, a mixture in proper proportions of natural sulphate of baryta, chloride of manganese, and coal, is transformed under the influence of a high temperature, into insoluble sulphide of manganese, and chloride of barium, which is easily separated by washing. The reaction may be represented by the formula—

$$BaO,SO_3 + MnCl + 4C = BaCl + MnS + 4CO.$$

"A similar reaction applies equally well to the chloride of iron, which constantly accompanies the chloride of manganese.

"The coal intervenes always as a deoxidizing agent, and is converted into carbonic oxide.

"After several preliminary trials, rendered necessary by the impurities of the materials employed, the correct proportions were determined upon. The results are beyond my expectations, inasmuch as I am now able to transform native sulphate of baryta into chloride of barium without a loss of more than 3 to 4 per cent. of sulphate of baryta lost or undecomposed.

"Here is the practical mode of working: The transformation is effected in large reverberatory furnaces, similar to those employed for decomposing common salt in soda works, with a hearth divided into two compartments by a low wall. When these furnaces have been heated for a certain length of time, the portion most remote from the fireplace is charged with a finely-pulverized mixture of native sulphate of baryta and bituminous coal; and above it there is poured the liquid residue from the manufacture of chloride, the free acid of which has been previously saturated with chalk or, better still, with native carbonate of baryta. The mixture is well stirred, and is thickened by the heat. When it has become a thick paste it is passed over the partition wall, with proper iron tools, into the compartment near the fire. There the mass becomes swollen and soon disengages small gas jets of carbonic oxide, similar to those produced at a certain period of the soda manufacture, but, in this case, having a green tinge due to the baryta. After an hour of calcination at a red heat, the semifluid paste, which has a little more consistency than that of crude soda, is removed from the furnace, and, when cold, forms a black mass of chloride of barium, with the sulphides of manganese and iron, and a small proportion of hyposulphite of baryta. After several days of exposure to the air, the mass becomes disintegrated, and the hyposulphite passes to the state of sulphate of baryta. The substances are then lixiviated with hot water in an apparatus disposed like that for crude soda.

"The liquors are a clear solution of nearly pure chloride of barium. Should there be a slight excess of sulphide of barium, causing a yellow coloration, there is poured in, until complete decoloration, a solution of chloride of manganese (residue of the manufacture of chlorine) which has been deprived of iron by digestion with powdered carbonate of baryta. Conversely, any excess of chloride of manganese is separated with sulphide of barium. Thus, we see that there is no practical difficulty in obtaining a very pure chloride of barium.

"Such is the method followed in my works for utilizing the residue of the manufacture of chlorine.

As it is of great importance, I shall give a few more details.

"The solution of chloride of barium, obtained from the raw product, marks 24 or 25° Bé. When it has been purified in the manner indicated above, chamber acid (sulphuric), diluted with water to mark 30° Bé., is poured into it as long as a precipitate is formed. The whole is then well stirred and let to stand. The sulphate of baryta is rapidly deposited, and the syphoned liquors constitute a hydrochloric acid marking 6° Bé.

"The artificial sulphate thus obtained is washed in a methodical way, in order to remove the last trace of free acid. It is then drained to the consistency of a firm paste in cloth filters, and the operation will be more rapid if the filters are pressed, or subjected to centrifugal action. When the paste has become thick enough, it is packed in barrels, and contains from 30 to 32 per cent. of water.

"It may be dried and moulded into lumps, like white lead. However, in the majority of cases, it is more advantageous to use it in the pasty state, because, once dried, it does not reacquire the same degree of comminution it possessed at the time of its precipitation.

"If I insist upon this method of utilizing the waste of the manufacture of chlorine, it is because it appears to me as presenting many economical results. Thus, in the preparation of satin paper hangings and of glazed pasteboard, the artificial sulphate of baryta, under the name of *blanc fixe*, has found its place. Its consumption extends considerably for distemper and silicious painting, and for calsomining ceilings. The actual production of my works amounts to 2000 kilogrammes per day.

"This substance possesses an unexpected property, upon which I shall insist: it seems to form a slow, but intimate, combination with the soluble alkaline silicates, and with these salts forms pigments of unmatched whiteness, possessing a certain lustre, and entirely unacted upon by sulphuretted hydrogen. It may also be employed for fixing other colors. A paint made of a mixture of zinc white and blanc fixe, acquires such an adherence and durability, that it may be safely applied upon old oil painting. Such a result is of the greatest importance for Paris, London, Brussels, and other large cities, where carefully built dwellings are covered with expensive oil paintings, which require to be often renovated."

SECTION II.

BLUE COLORS.

The same substances which furnish blue present a very great many tones of that color. It will also be remarked that the purest and brightest blues are, at the same time, the most durable.

The *blues* most frequently used in painting are: *Ultramarine*, *Cobalt blue*, *Prussian blue*, *mineral blue*, *Indigo*, various kinds of *azure*, etc.

§ 1. *Prussian blue.*

This color was discovered in 1720 by Diesbach, of Berlin, and then studied out, theoretically and practically, by many chemists and manufacturers.

Prussian blue is now considered by all chemists to be a combination of cyanogen with iron in two states of oxidation; that is to say, a combination in variable proportions of protocyanide and sesquicyanide of iron with a little water.

As the composition of Prussian blue is not constant, and may vary with the proportions of the two cyanides of iron, this pigment is found in the trade, possessing a variable intensity of coloration. This diversity is due not only to the variable proportions of the cyanides, but also to the mode of preparation, the quality of the raw materials, and to the care in the manufacture. The average composition of Prussian blue is: three equivalents of protocyanide of iron, two of sesquicyanide, and nine equivalents of water.

When pure, and recently precipitated, it is in the shape of blue flakes, which are so deeply colored that they appear black. After drying, the lumps are blue-black, with a reddish reflex.

The pure article of the laboratories is made by pouring a solution of yellow prussiate of potash (ferrocyanide of potassium), into a salt of sesquioxide of iron. This process is too long and expensive to be used in the arts, and other methods are employed, one of which begins with the preparation of the cyanide of potassium, by the calcination of carbonate of potassa with animal substances.

1st. *Manufacture of Ordinary Prussian Blue.*

A. *First process.*—The animal substances ordinarily employed in the manufacture are: dried blood, hair, wool, waste from skins and leather, flesh, animal oils, soot, and bone black, etc.

Dried blood is preferred for the preparation of the cyanide. The fresh blood is rapidly evaporated in cast or sheet-iron pans, and the mass is constantly stirred with an iron tool, until it is entirely clotted. The drying is then finished in the sun, and the powdered material is kept for use in open vessels.

10 parts of the powdered blood are moistened with 1 part of pure carbonate of potassa dissolved in water, and 1 per cent. of iron filings are added to the mixture, which is heated in a cast-iron pan for seven or eight hours, and at a red heat. During the first hours of the calcination, abundant fumes are disengaged, which possess a very disagreeable smell, and are afterwards replaced by bright and reddish-white jets of flame. The mixture is stirred, and, when it is in the state of quiet fusion and does not emit jets of burning gases, the cover is put upon the kettle, and the heat continued for two hours more. The cakes of the cooled product are lixiviated with hot water until all the soluble matters are removed.

The resulting *blood lye*, as it is sometimes called, is a light yellow, and smells of prussic acid strongly. It is not a solution of pure cyanide of potassium, but contains, besides, a certain amount of carbonate of potassa, of sulphates and phosphates of potassa and lime, of sulphide of potassium, etc.

This concentrated and filtered lye is poured by degrees into a hot solution of one-half part of pure sulphate of iron, and a variable proportion of alum, depending on the quality of the blue desired. The quality more generally called Prussian blue is obtained with one part of alum to seven or eight parts of sulphate of iron. The ordinary blue employs one part of alum to two or three parts of sulphate of iron;

and the inferior qualities are made with equal parts of sulphate of iron and alum.

At each addition of the cyanide lye to the iron solution, there is an abundant production of hydrosulphuric and carbonic acids, and the escape of these gases is aided by stirring the liquor with a wooden rod. The precipitate is brownish-green, and is washed with pure water, until it turns entirely blue.

After settling, and decanting the liquors, the blue precipitate is placed upon a cloth filter, where it is washed with water holding a small proportion of sulphuric acid. The drained blue is then pressed in boxes, in order to remove the greater part of its water, and the thick resulting paste is divided into rectangular blocks, which are dried in the dark, or in a stove-room, the temperature of which should not be above 25° to 30° C.

Prussian blue, in the opinion of Mr. Bourgeois, is the next in purity of tones after ultramarine and cobalt blues; and, although it is inferior to these in durability, it contains much more coloring power—from ten to eleven times, with equal volumes. It is to be regretted that all the alkalies alter Prussian blue, so that, if it be combined with other alkaline pigments, it may rapidly change or disappear. Mr. Bourgeois indicates a process for ascertaining the presence of Prussian blue in suspected samples of lazulite and cobalt blues, which is based upon the discoloration of Prussian blue by alkalies. A pinch of ultramarine or cobalt blue, is digested for about one hour in a small quantity of lime-water. The presence of Prussian blue will be detected by the lime-water turning lemon yellow, and by an ochreous precipitate.

Large quantites of Prussian blue are used by house painters and decorators, and by manufacturers of paper hangings.

Of all blues, Prussian blue is the most intense. Mixed with white lead, the hue is slightly greenish. A mixture of one gramme of Prussian blue and ninety grammes of white, produces a sky blue; two hundred grammes of white, and one of blue, give an azure white. In order to judge well of the beauty of a Prussian blue, it should be incorporated with from fifty to one hundred times its weight of fine white lead. Mixed with from fifteen to twenty times its weight of chrome yellow, it produces handsome greens, not very lasting however. Prussian blue is employed either with glue size or oil; but, in the latter case, it should not be kept too long without being applied, because it becomes thick and does not flow well under the brush. The pure blue ground in oil produces velvety blacks which could not be arrived at by the employment of black pigments. We should remark that old damp walls destroy the color of Prussian blue, by the nitrate of lime they contain. There is produced by double decomposition, a ferrocyanide of calcium, and a nitrate of iron.

B. *Second process.*—We have seen that in the first process, a lye of impure cyanide of potassium was prepared. As this operation is unwholesome, on account of the deleterious gases produced, other modes of manufacture have been adopted, which allow of the manufacture of Prussian blue in inhabited places. The ferrocyanide of potassium (yellow prussiate of potash) is employed, and may be prepared in a special locality, in the following manner:—

This second process has nearly everywhere taken the place of the first. The mixture consists of seventy-five parts (kilogrammes for instance) of good carbonate of potassa, fifty parts of horn or leather waste, and three of iron filings. The potash is introduced first into a furnace which we shall describe further on. When it has arrived at the point of igneous fusion, the iron filings are introduced and mixed in the mass with an iron tool, which has been heated red beforehand, otherwise the stuff attaches to it and renders the operation difficult.

When the mass is thoroughly in fusion, a shovelful of horn waste or animal charcoal is thrown into it every ten minutes. At the last addition of animal matter, a strong heat is maintained for about one and a half hours, and the operation is completed when jets of carbonic oxide burn on the surface of the bath. The substances are then removed with red-hot iron ladles, and deposited in iron kettles, where they are afterwards boiled with water. After two boilings, settlings, and decantations, the residue is removed and again thoroughly washed in cloth sacks. All the liquors are evaporated to the proper degree, and, by cooling, give crystals of ferrocyanide of potassium, which are rendered purer by another solution and crystallization.

With the proportions indicated above, the product is from seventeen to twenty parts of ferrocyanide.

The mother liquors are evaporated to dryness, and their potassa is used for another operation. The charred residue is of no value.

The calcination of the substances is effected in a reverberatory furnace having the following dimensions: height of arch 0.50 metre, over the horizontal bed or hearth, which is 1 square metre. The fireplace is sideways, $0^m.21 \times 0^m.48$, and bridge wall is $0^m.27$ or 0.5 metre wide. On top of the arch, there is an opening covered with a sheet-iron hood and chimney. The wide working front of the furnace is closed by two cast-iron doors, having on their line of junction a hole large enough to introduce and operate the stirring hooks.

The animal charcoal is prepared either in cylinders or in cast-iron pots, or in muffles of the same metal. We shall also indicate a few of the more recent processes which have been proposed for the manufacture of ferrocyanide of potassium or of Prussian blue.

2d. *Brunnquell Process.*

Mr. R. Brunnquell, who has managed for a long time a manufactory of ferrocyanide of potassium, near Bremen, has published in Berlin a long memoir on this subject. We cannot reproduce it entirely, but we shall give some extracts taken from the *Technologiste*, vol. 18, pages 243 and 291.

Let us state first that the author has examined several processes for the manufacture of ferrocyanide of potassium, and particularly, the one in which the ammonia produced during the carbonization is brought in contact with potassa and charcoal, at a high temperature. He observes that, however advantageous these processes may appear, they are not well adapted for manufacturing operations.

Considering the defects of the actual process, there remains for the manufacturer to diminish the loss by a careful attention to certain details of the operation. There are two ways of arriving at this result: First, to aid, as far as practicable, the secondary formation of cyanogen (by ammonia and incandescent charcoal); second, to avoid the loss of potassa by using pure animal substances, and by preventing the contact of the ashes of the fireplace. The author, from his own experience, indicates the following mode of operation.

A horizontal reverberatory furnace* is generally adopted at the present time, the hearth of which is made of a cast-iron dish, 10 to 12 centimetres deep, 1.5 metres in length, and 1.2 metres wide, and several centimetres thick. The furnace is so constructed that the working space is no greater than is necessary, and the arch is as flat as it is possible to build it. The flue from the fireplace has a damper, by which the flame may be made to pass into an opening connected with a metallic hood and chimney. This arrangement saves the men from being annoyed by the gases and by too much heat. The author enlarges on the advantage of heating by gases, by which oxidization and ashes are prevented. The flame may even be made deoxidizing. There is certainly no manufacturer who has not observed the great quantity of ashes deposited after twenty-four hours in the cast-iron dish of a newly heated furnace, especially, when the draft is good. We know also, how deleterious is the

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* These furnaces, notwithstanding many defects, present three important advantages: I. There is a considerable economy of fuel; II. The work is easy and rapid. Where, in other furnaces, 4 charges were a day's work, in these, from 7 to 8 charges, each double the former in weight, were effected; III. The furnaces cost less and last longer.—In England, where fuel and iron are cheap, and labor high, the metallic egg-shaped furnaces are used, and the stirring is done by power. No other but carbonized animal substances can be charged there, and they must be mixed with the potassa in the furnace, whereas their mixture is more thorough in revolving cylinders.

action of these ashes upon the contents of the bath, especially when peat or bituminous coal is burned.

With a furnace of the above construction, the author proposes a mode of operation, which has already been employed in several works, and which may be described as follows: The charge is composed of 100 kilogrammes of potash, two-thirds of which is from the evaporated mother liquors, and one-third of fresh potash; 20 kilogrammes of animal charcoal obtained by the carbonization of substances poor in nitrogen, and the nature of which is not well adapted for a direct treatment; from 65 to 70 kilogrammes of pure animal matters, as dry as practicable; and 8 kilogrammes of iron. The fire is urged until all the potash is thoroughly fused, which state is more rapidly reached with the aid of two or three stirrings. Then the ash pit is closed* and the damper turned on for charging one-half of the animal charcoal. The fire is urged again, and the stirring is continued vigorously, until the mass has acquired the proper consistency and potassium is produced, which is ascertained by the formation of blue flames of oxide of carbon, and by a peculiar white cloud of burning vapor of potassium. In this state, the fused mass is in the proper state for transforming into cyanogen the ammonia disengaged from the animal substances. The latter are then put in, those richer in nitrogen first, but not in large pieces or in considerable quantities, which would prevent their rapid sinking and their equal distribution in the bath, and would produce gas too rapidly

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* When the furnace is heated by means of a gas generator, a reducing flame will be obtained by diminishing, or stopping entirely, the entrance of the air necessary to complete combustion.

at one spot. The ammonia will not have time to be transformed. When the 65 to 70 kilogrammes of dried animal substances have been charged in, the mass begins to be hard and dry, and difficult to fuse. No time should then be lost in adding the remainder of the animal charcoal, which, being in a fine powder, is more readily incorporated, and reduces the cyanide of potassium (cyanate of potassa?) already formed. Lastly, after another thorough stirring, the working door is closed for a little while, and the contents of the furnace are rapidly removed into an iron vessel, which is immediately covered.

It does not seem advantageous to work at any one time with charges much greater or less than the indicated proportions; but the author does not say that these numbers are the only correct ones, and the manufacturer, in certain cases, will do well to modify them. Mr. Brunnquell has made many experiments for the purpose of establishing to a certainty, the composition of the charges in the ratio of the nitrogen held by the animal substances; but he soon found out that the result depended upon so many other circumstances, which often could not be explained, that it was impossible to establish rules adapted to all modifications. The manufacturer who has a careful foreman, who can be trusted, should give him a certain liberty of action in this respect. Practice will point out the time when the charge is completed, and does not require any new additions; or how different animal matters should be treated. Thus, hair and leather waste render the mass hard and dry; whereas with sinews, rags, etc., the charge remains fluid and easily worked.

Mr. Brunnquell remarks, and rightly so, that the value of the raw materials is not in a direct ratio with their per cent. of nitrogen. A substance with twice as much nitrogen as another, may have a value more than double, because with the same loss of potassa, the same labor, and the same consumption of fuel, the production of ferrocyanide is much greater. Old shoe leather should be employed with moderation, since the author, after careful washings, ascertained that it contained a large proportion of sand and other impurities.

In regard to the addition of iron filings or turnings, Mr. Brunnquell states that it does not increase the yield, but saves the cast-iron vessels in which the operation takes place. It results from experiments made by Mr. Fleck, that a cast-iron crucible will stand 100 operations without the addition of iron. If the latter be introduced into the charges, the vessel will last through from 350 to 400 operations. The iron tools which are constantly exposed to the action of the fused mass, are always covered with a coat of sulphide of iron. On the contrary, the iron scraps introduced during the operation, have scarcely the time to be transformed into sulphide before they are removed from the furnace.

At all events, the whole indicated proportion of iron scraps should be added at the beginning of the operation, with the animal charcoal. Certain manufacturers put in the iron scraps during the last period of the heat, and cannot expect to save their crucibles and cast-iron hearths. The author learned that, in a German establishment, it was considered as very important to let the iron scraps become oxidized beforehand; but he made no direct experiment, and, should there be any advantage in the precaution, it would be more simple to use pure spathic iron or iron scales.

Here is a little more advice on the manner of treating the calcined charges. When cold, they are coarsely broken, then digested for twenty-four hours in water at the temperature of from 50° to 60° C. with frequent stirrings, and lastly, boiled. After settling, the liquor is decanted, and the residue is washed with water. The other manipulations present no difficulty. The main point is the manner of working the charge, and a peculiarity of this manufacture is, that it is more easy to obtain a good product, than a great deal of it. The only difficulty in the way of the quality, is the separation of the sulphate of potassa from the crude ferrocyanide, and the best method consists in a complete reduction during the calcination of the charge.

The process which we are going to describe, and which was experimented upon by the author conjointly with Mr. Weber, consists in transforming ammonia into cyanide of ammonium, by heating the former substance with charcoal or other carbon materials. A distinguishing feature is the transformation of the cyanide of ammonium thus obtained, into cyanide of potassium, and that of the latter into ferrocyanide by the wet way. The operation consists in passing the gases and ammonia, produced by the carbonization of the animal substances, through tubes holding incandescent charcoal. The ammonia becomes cyanide of ammonium, which is put in contact with an aqueous solution of potassa and with an iron compound. The result is ferrocyanide of potassium. Here are the principal advantages of this process:—

I. There is no great loss of potassa, and the expense of revivifying this alkali is entirely done away with;

II. It is possible to replace potassa by soda, which is much cheaper;

III. It is possible to employ bones, the residuary black of which is generally sufficient to cover the cost of the bones and of the calcination. Therefore, the ammoniacal gases cost nothing;

IV. It is possible to save for a further operation the ammonia which has escaped transformation into cyanide during the calcination. The secondary ammoniacal salts may also be utilized, by adding them, with a certain proportion of lime, to the raw materials.

Several questions relating to the process of manufacture have been resolved by the author, as follows:—

1. The transformation takes place without difficulty, and on a scale sufficiently large to base upon it a system of preparation of cyanogen compounds. As a proof of the possibility of the reaction, we may cite the production of the cyanide of ammonium from ammonia and carbonic oxide, or from the gaseous nitrogen oxide and alcoholic vapor under the influence of spongy platinum.

2. The gases, other than ammonia, which are produced at the same time during the carbonization, are not an obstacle to this process of manufacture.

3. The transformation of the cyanide of ammonium into ferrocyanide of potassium, is effected without loss.

The easiest method of operating this transformation would be that proposed by Mr. Binks, that is, with an aqueous solution of potassa. But we cannot do so, because the carbonate of potassa is not decomposed, either by hydrocyanic acid or by cyanide of ammonium.* Caustic potassa, on account of the excess of carbonic acid in the gases, cannot be used. We must, therefore, have recourse for this decomposition to intermediary substances, and the author chooses the sulphate of protoxide of iron. If cyanide of ammonium, or hydrocyanic acid and carbonate of ammonia, be passed through a solution holding an excess of sulphate of iron, sulphate of ammonia and cyanide of iron are produced. We thus obtain a double result: first, all the ammonia is collected in the state of sulphate, which pays largely for the expense of the iron salt; second, the cyanide of ammonium is instantaneously transformed into an insoluble and fixed compound, which, after a treatment with the carbonates of potassa or soda, may furnish a ferrocyanide of either of these bases.

During the process of manufacture, the carbonization is effected so as to expel all the nitrogen in the gaseous form, instead of preserving it in the carbonaceous residuum, as in former methods. If bones be employed, the quality of the resulting bone black should be considered, and it matters little whether or not a small percentage of nitrogen remains in it. We

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* More recently the author has made several direct experiments which clearly prove that carbonate of potassa, either in solution in water, or at a high temperature, decomposes cyanide of ammonium completely. But, as he has never been able to realize this transformation in his experiments on a large scale, and has always remarked that hydrocyanic acid was disengaged, especially when the alkaline liquors were boiled, Mr. Brunnquell considers this fact as a positive proof that carbonic acid has intervened, and that, instead of cyanide of ammonium, hydrocyanic acid (with a little undecomposed carbonate of ammonia) was obtained. Therefore, theoretically speaking, there must be a way of transforming at once all the nitrogen into cyanogen.

know that the good quality of bone black depends on the following conditions: the bones employed should not be deprived of their fat; the carbonization must be complete, and effected without gaseous pressure. When other raw materials are used, it is important to obtain all the nitrogen; therefore, a first carbonization transforms them into a charcoal easily pulverized, which is then thoroughly mixed with slaked lime, and calcined again. The residue is a very good manure or compost.

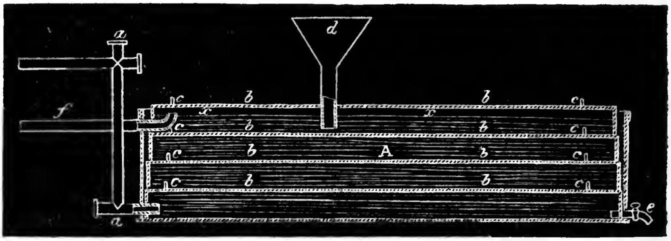
The carbonizing furnaces are disposed like those of gas works, and the number and the sizes of the retorts are made to suit the importance of the manufacture. The outlet pipes all dip into a common horizontal main, where the distilled animal oil is condensed, and there is formed a hydraulic joint, which produces a certain pressure. All the products thus become mixed before they reach the calcining tubes made of fire clay. There is also the advantage that the flow of gases is quite regular, because the small volume of gases produced by a retort at the end of the distillation, is counterbalanced by the large volume of gases issuing from another retort which has been recently charged. If we suppose that three retorts are employed, and that the carbonization of a charge lasts six hours, one retort will be filled every two hours. The pipes connecting with the hydraulic main should be provided with stopcocks in case an accident should happen. They should also be at least six centimetres in diameter, short, and easy of access in every direction.

The transformation of the ammonia into cyanide of ammonium takes place when the gases pass through the fire-clay pipes, which are heated to an intense red heat, and filled with wood charcoal, broken into pieces of the size of walnuts. Numerous trials have proven that iron pipes cannot be used for this purpose, because, when cyanide of ammonium, or hydrocyanic acid, or cyanogen are brought into contact with iron at a red heat, they split into their elements, and form a carbide of iron. In three experiments made with gunbarrels, not a trace of cyanide of ammonium was found. The author tried to employ in this manufacturing process, an iron cylinder, by protecting its inside with a carbonaceous surface obtained by the calcination of several coats of tar. But the results of the working operation were far from satisfactory, since the yield was but 4 per cent. This was possibly due to the fact that he had not, at that time, ascertained the great proportion of carbonic acid contained in the gases; and that the caustic potassa, intended for the absorption of the cyanide of ammonium, had been transformed into carbonate, and even bicarbonate. The best process for protecting the iron tubes was found to be several coats of a mixture of clay and ox blood, gently heated after each successive coat. During the first experiments with sulphate of iron, instead of a solution of potassa, too much heat was applied, and the iron pipes were burned. Although it does not appear entirely impossible to use metallic pipes, those made of fire clay seem to be preferable in every respect. These pipes have a smaller diameter than the retorts, and their extremities are so disposed as to receive cast-iron joints. The smaller their diameter and the greater their length, the better it is for the operation. Those used by the author were 10 centimetres in diameter and 2 metres long. The internal disposition of the furnace is also that of furnaces for gas retorts, where the greatest possible number of retorts are to be heated throughout their whole length, with the smallest consumption of fuel. A very good furnace is that of Croll for gas, with the combined employment of clay and cast-iron retorts.

With this disposition it has been possible to heat seven retorts and seven pipes with one fireplace. The filling of the pipes with charcoal is not absolutely necessary, because the other gases accompanying the ammonia may furnish the carbon for the cyanogen; but charcoal, on account of its porousness, aids in the transformation. The extremities of the pipes are closed with perforated disks of fire clay, which prevent the joints from becoming obstructed. Before the gases are allowed to pass through, the pipes should be of an intense red heat. In addition to the ordinary losses of manufacture, there are undecomposed tarry vapors, which dirty the liquors. A very intense red heat is the temperature necessary for the formation of cyanogen. As in previously described processes, the yield depends on regularly conducted operations.

We have seen that the transformation of the cyanide of ammonium into cyanide of potassium, and then into ferrocyanide of potassium, is effected by the intermediation of the sulphate of iron. The only difficulty in the practical operation is to arrive at a complete absorption of the cyanide of ammonium in the solution of sulphate of iron, and that without a strong pressure of gases, which not only impairs the quality of the bone black, but causes losses of a portion of the gases through leaks in the apparatus. The author uses, for this purpose, apparatus which is very simple and permits of regulating at will the rapidity of the operation. Let us suppose a box, about 2 metres long, 60 centimetres wide, and 20 centimetres deep, in which are placed four flat, shallow pans, 5 centimetres high, and put one on top of the other in an inverted position (Fig. 47). On the bottom of each pan, towards one of the ends, there is a narrow opening. The box is

Fig. 47.



filled with the liquor, and the mixture of gases, which is introduced below the first pan, expands until it gains the opening. It then passes into the second pan, and, in the same manner, into the third and fourth. Theoretically speaking, there is constantly a layer of gases, of 4 × 1.20 metres = 4.80 square metres in area, in contact with the liquid, and the distance followed by the gases is 4 × 2 metres = 8 metres, under a pressure of only 0.20 metre of water. The box is also provided with a stopcock for removing the liquors, a funnel which dips a little below the level of the liquid, and an outlet pipe for the washed gases, which are afterwards burned under the fireplace. In order to prevent explosions the gases to be burned are made to pass through a small box filled with fine metallic gauze. Should a precipitate take place in the liquors, it is recommended to employ a stirring apparatus with blades in each compartment of the box, and the vertical shaft of which passes through a stuffing-box.

In the figure, *a a* is the pipe which conducts the gases into the box; A, sheet-iron box; *b b b b*, sheet-iron inverted pans; *c c*, handles for moving the pans; *d*, funnel; *f*, outlet pipe for the gases; *x x*, level of the liquor.

Instead of a large absorbing apparatus, it will be more advantageous to employ two smaller ones, so disposed as to pour the liquors from one into the other. In this manner the sulphate of iron will be entirely precipitated without loss of cyanide of ammonium. The liquor running from the first box will, therefore, hold only sulphate of ammonia in solution, cyanide of iron in suspension, and a small proportion of hydrated oxide and sulphide of iron.* The sulphate of ammonia is separated from the filtered liquors by evaporation, and is sold to the alum makers, or is mixed with lime and animal substances for the production of cyanogen. The precipitate of cyanide of iron is boiled with potassa and transformed into ferrocyanide. Lastly, the residues of iron are either thrown away, or dissolved in hydrochloric acid, to be used instead of sulphate of iron.

There is no difficulty in the preparation and crystallization of the ferrocyanide of potassium, because the materials employed are quite pure. If the iron precipitate has been sufficiently washed, and then boiled with a solution of purified potassa, the liquors contain but a small proportion of carbonate of potassa, besides the ferrocyanide. The author believes that soda may be employed, and experiments on a large scale have furnished a pure yellow ferrocyanide of

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* For the preparation of 300 parts of ferrocyanide of potassium, we need 187.3 parts of cyanide of ammonium. The latter requires for its formation 600 parts of sulphate of iron, and produces 243 parts of sulphate of ammonia.

sodium, but in small crystals. The iron deposit left after the treatment with the alkalies, should be washed and drained. The washings are kept for making fresh solutions of potassa. The mother liquors are also put to the same use.

If we compare the old and the new processes, we find:—

First, that in the latter there is a saving of labor. The fusion of the potassa and animal matters, which requires two workmen, is entirely avoided, and one workman is sufficient for two carbonizing furnaces and a great many clay pipes, since these require to be opened but once every two or three days for the purpose of adding a little charcoal. The labor required for the treatment by the sulphate of iron is much less than that required for lixiviating the carbonized cakes of raw materials. Moreover, the labor entailed by the revivification of the salts of the mother liquors is entirely obviated.

Second, the consumption of fuel in the new process is somewhat greater, because the formation of the cyanogen is slower. But, supposing that the consumption be double, this inconvenience is more than counterbalanced by the advantages of the method.

It is acknowledged that the process presents certain difficulties, which may, however, be overcome; but the great saving in potassa, and the possibility of substituting soda for it, are very important economical results.

In concluding, the author remarks that the method he proposes, that is, the production of the cyanogen before its combination with the fixed alkalies, may possibly lead to the employment of atmospheric air. During the experiments made on the production of cyanogen from the nitrogen of the air, MM. Wœhler, Erdmann, and Marchand have remarked that this preparation succeeds only in the presence of steam or of hydrate of potassa. This observation, and other analogous ones, have caused many chemists to suppose that there was always a formation of ammonia. Direct experiments have also proven the production of ammonia from nitrogen and steam in contact with red-hot charcoal. Mr. Fleck has communicated to the author the results of such experiments, by which he obtained quite a large proportion of ammonia; but in several cases, and without ascertained causes, no ammonia was formed. It seems that this mode of formation should be studied more thoroughly, and directly, that is, for instance, by mixing with nitrogen, variable measured proportions of steam, and then transforming the ammonia thus produced into cyanide of ammonium by the process indicated. We shall thus avoid most of the practical difficulties up to the present time encountered, in the preparation of the cyanide of potassium from the nitrogen of the air, for instance, among others, that of the rapid destruction of the clay pipes by the fused potassa.

3d. *Karmrodt Process.*

In the Bulletin of the Society for the Advancement of Arts, Berlin, 1857, there is a memoir of Mr. C. Karmrodt upon the ferrocyanide of potassium and its manufacture by a new process, which we shall reproduce in part.

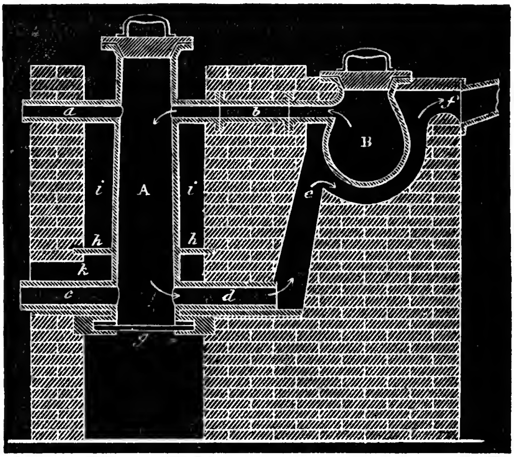
The author points out the destructive action of the vapors, disengaged from wood and animal substances, upon the cyanide of potassium in the nascent state, and states that experiments made with charges of 250 kilogrammes of potassa and 250 kilogrammes of the substances mentioned below, gave the following yields in ferrocyanide of potassium :—

10 charges	with	woollen rags,	15.22	per cent.	of ferrocyanide.
10	"	" horn waste,	16.26	"	"
10	"	" cow's hair,	11.94	"	"
10	"	" leather waste,	13.52	"	"
10	"	" good charred horn,	16.23	"	"
10	"	" woollen rags,	17.57	"	"

Showing that only from one-seventh to one-third of the nitrogen present in the raw materials was utilized. Mr. Karmrodt demonstrates the advantages resulting from the previous carbonization of the raw substances, and then passes on to the description of his new process for the manufacture of ferrocyanide of potassium, as follows :—

In order to combine in the most advantageous manner the production of the cyanide of potassium with ammoniacal gases, and the working of the charge with the nitrogenized charcoal, I have invented the

Fig. 48.



furnace which is represented in the vertical section in Fig. 48.

The cast-iron cylinder A, for calcining, is 1.20 metres long and 0.15 metre in diameter on top, the lower portion being a little larger. Its thickness is 25 millimetres, and it carries four tubes, *a*, *b*, *c*, *d*, cast with it, 5 centimetres in diameter and from 36 to 40 in length. The tube or pipe *b* is connected by flange joints and another small pipe, with the carbonizing vessel B, which is pear-shaped, and about 30 centimetres in diameter. The pipe *d* penetrates the brick flue *e*, which continues around the vessel B, and ends at *f*. The other pipes *a*, *c*, are employed for cleaning those which are opposite, and are generally closed with a plug of clay. The carbonizing vessel B, and the calcining cylinder A, are both closed with a cover which may be made gas tight. Under the cylinder, there is a square iron frame in which the register *g* slides horizontally. At about 30 centimetres above, there is also an annular grate *h h*.

When the calcining cylinder is charged with alkalized charcoal, it is heated with a charcoal fire. Some time afterwards, the space *i i* is closed with an iron cover, and the draft takes place through a flue placed under the pipe *b*, which thus establishes a heating system common to A and B. When the calcining cylinder A has been brought to a red heat, the animal substance is quickly introduced into the carbonizing vessel B, which is immediately closed with its cover luted on. The gases produced by the carbonization escape through the pipe *b*, pass through the whole length of the cylinder A, and coming out at *d*, are burned under the vessel B, and increase its temperature considerably. By this disposition, all the products of the combustion of the fuel and of the carbonization of the animal matters, are expelled through the flue *f*, and go to the chimney, or are utilized for evaporating the liquors. No disagreeable smell is disengaged and the carbonizing operation lasts from three-quarters of an hour to one hour and a quarter.

When the carbonization is completed, and when the gases passing through the cylinder have formed a certain portion of cyanide of potassium, the register *g* is removed, and the contents of A fall into a sheet-iron box placed below, and which is closed tight. After cooling, the materials are thrown into water by small portions at a time, because, should all the charcoal saturated with cyanide of potassium be thrown at once into the water, the elevation of temperature would be such as to decompose a large portion of the cyanide.

The water is then slowly heated up to from 75° to 80° C., and the charcoal is separated from the solution by means of a metallic sieve. A well-washed charcoal may be used for another operation, or it is used as fuel, and its ashes are carefully lixiviated, because they are rich in potassa.

The alkalized charcoal is prepared as follows: In an iron kettle, 20 parts of good Russian potash are dissolved in 10 parts of water, and there is mixed in it the wet, but washed, precipitate resulting from the mixture of 8 parts of sulphate of iron and 6 parts of potash. 30 parts of charcoal, broken to the size of a filbert, are then stirred with the mixture, and the whole is dried at a moderate temperature. Coke may be cheaper than charcoal, but the lixiviation requires more water, and its ashes have scarcely any value. The sulphate of potassa resulting from the precipitation of the sulphate of iron, is used in the manufacture of alum.

Mr. Karmrodt has made experiments with the furnace above described, and the results are:—

I. *By using each time* 1.5 *kilogrammes of Carbonate of Ammonia (crude and yielding* 21 *per cent of Nitrogen).*

	Ferrocyanide of potassium obtained with the carbonate of ammonia.		*Utilized nitrogen.*	
	Per 1.5 kilog.	Per cent.	Per cent.	Approximately.
1.	0.500 kilog.	33.3 per cent.	31.74 per cent.	$\frac{1}{3}$
2.	0.625 "	41.5 "	39.68 "	$\frac{2}{5}$
3.	0.562 "	37.5 "	35.71 "	$\frac{1}{3}$

The greater proportion of assimilated (utilized) nitrogen in these experiments, in comparison with the results obtained with gunbarrels, is possibly due to the greater surface of reacting substances, and to the pressure of the gases during their passage.

II. *With Animal Substances.*

The alkalized charcoal of these experiments was prepared with 15 kilogrammes of horn charcoal (yielding 7 per cent. of nitrogen), and 10 kilogrammes of potash. After the addition of the washed precipitate resulting from 4 kilogrammes of sulphate of iron with 3 kilogrammes of potassa, the dried mixture weighed 22 kilogrammes.

In each operation there were 5 kilogrammes of this alkalized charcoal, corresponding to 3.4 kilogrammes of horn charcoal, placed in the calcining cylinder; and it received the gases produced in the carbonizing vessel from 1.5 kilogrammes of horn (yielding 16 per cent. of nitrogen).

The nitrogen employed was therefore:—

a. In the alkalized charcoal . . .	238 grammes.
b. In the raw horn to be carbonized .	240
	478

which should have produced altogether 2.39 kilogrammes of ferrocyanide of potassium.

Ferrocyanide of potassium obtained with 1.5 kilog. of horn.	*Utilized nitrogen.*	
	Per cent.	Approximatively.
1. 770.31 grammes.	32.4	$\frac{1}{3}$
2. 664.06 “	27.9	$\frac{1}{4}$
3. 712.50 “	30.0	$\frac{1}{3}$

In these experiments, there remained in the carbonizing vessel 1.203 kilogrammes of horn charcoal, which, after fusion with potassa, gave 109.37 grammes of ferrocyanide of potassium. To sum up, the results were:—

1. 770.31 grammes of ferrocyanide = 154.06 grammes of nitrogen.
2. 664.06 “ = 122.81 “
3. 712.50 “ = 142.50 “
4. 109.37 “ = 20.31 “

2256.24 “ = 439.68 “

whereas the whole of the nitrogen employed was 3 × 478 = 1434 grammes.

III. *With Animal Substances, and the Alkalized Charcoal of* 30 *kilogrammes of Wood Charcoal,* 20 *of Russian Potash, and the Precipitate of* 4 *kilogrammes of Sulphate of Iron by* 3 *of Potash.*

In each operation, there were used 5 kilogrammes of alkalized charcoal, upon which were passed the gases of 1.5 kilogrammes of raw horn. The results were:—

1.	574.22 grammes of ferrocyanide	=	114.84 grammes of nitrogen.
2.	461.00	"	=	92.19	"
3.	457.03	"	=	91.41	"
4.	156.25[*]	"	=	31.25	"
	1648.50	"	=	329.69	"

The whole quantity of horn employed was 4.5 kilogrammes = 620 grammes of nitrogen. We see therefore, that in this series of experiments, the proportion of nitrogen utilized is about one-half of the whole.

Now, if we suppose that in the second series of experiments with animal alkalized charcoal and the same quantity of horn as in the third series, there were produced as much ferrocyanide of potassium as in the latter case, it would result that the overplus of 38.4 parts of ferrocyanide is due to the alkalized animal charcoal.

If we compare together the yields which should be obtained, we find that, with the alkalized animal charcoal, about $\frac{1}{6}$ of the nitrogen is utilized. Indeed, 10.2 kilogrammes of horn charcoal (at 7 per cent. of nitrogen) contain 710 grammes of nitrogen, which should have produced 3580 grammes of ferrocyanide of potassium, while the result was only 600 grammes.[†]

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[*] This ferrocyanide comes from the treatment of the charcoal left by the carbonization of 4.5 kilogrammes of raw horn, in three operations.

[†] Although, from the numbers admitted by Mr. Karmrodt, it would seem that the yields have been really those obtained at the end of the operation, we should remark that in the most careful mode of working, there are always losses which cannot be avoided, and which are sometimes due to unknown causes. The proportions of nitrogen indicated for various animal substances are average numbers. In order to facilitate the calculation, it has been assumed that ferrocyanide of potassium contains 20 per cent. of nitrogen, whereas the real proportion is 19.87 per cent.

Although this method for the manufacture of ferrocyanide of potassium is far from the desired perfection, we must admit, from the experiments, that it presents several advantages over the usual processes:—

1. A greater proportion of nitrogen is utilized.

2. The liquors, and the resulting commercial salt, are less impure than when the ordinary process of fusion is followed.

3. The loss of alkaline salts is small, while it is considerable in the method by fusion.

4. The residues are small.

A manufacturing establishment, working by this method, should have several furnaces of the pattern indicated, since the daily production of one furnace is only twelve kilogrammes of ferrocyanide of potassium.

It is possible to increase the dimensions of the apparatus, and to put four cylinders in one furnace, so as to produce fifty kilogrammes. A cheaper fuel than charcoal may be employed, and burned in a fireplace common to the four cylinders.

4th. *Schinz Process.*

In the apparatus of Mr. C. Schinz, cyanide of potassium is formed by the contact of potassa with nitrogen, or with the products of the distillation of nitrogenized substances in closed vessels.

Figs. 49, 50, and 51 represent the apparatus. *a*, feeding cast-iron cylinder placed on top of the apparatus, and closed tight with the cover *b*. *c c*, cast-iron plate supporting *a*, and perforated with a hole corresponding to the diameter, in the clear, of the cylinder. Underneath is an iron frame in which slides a register or damper *e*, having a hole *e'*, which may be made coincident or not with the opening of the lower plate. This damper is moved by an arrangement *f* of rack and pinion.

Fig. 49.

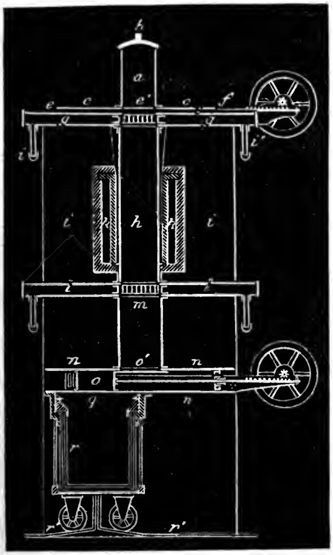


Fig. 50.

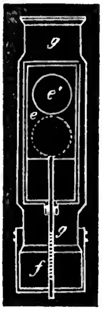
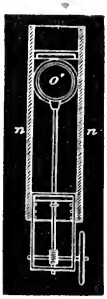


Fig. 51.



The lower part of this iron frame covers a flue *g*, which communicates through a circular grate with a vertical retort *h*, placed immediately below the opening already mentioned. The circular grate is movable, in order to be cleaned when necessary.

The furnace is placed under the flue *g g*, and from this flue and through the sides *i i*, of the furnace, there are two gas pipes *i' i'*, one on each side.

The vertical retort *h* is made of sheet iron, and is enclosed in sand kept in a special space, so that the retort may expand and contract when heated or cooled. The fireplace, which is lined with fire-bricks, is placed around the lower part of the retort, and is separated from the sand by a cylinder *k k*, of refractory clay. The retort *h* is supported by another flue *l l*, similar to *g g*, and is connected by means of a grate with another cylinder *m*, which is immediately below the retort *h*, but has a diameter a little larger. The cylinder *m* receives the substances delivered into it, and, being hermetically closed, protects them from contact with the air while they are cooling off. It is supported by a rectangular box *n n*, in which moves, by rack and pinion, a piston which closes or opens the aperture *o*, placed sideways of the axis of the apparatus. The receiver *q* rolls on small wheels, and its top fits close to the piston-box *n n*. A cylindrical metallic sieve *r* may be put in, or removed from the receiver *q*, by means of handles. A system of levers raises the rails *r′ r′*, and causes the receiver to be firmly pressed against the box *n n*.

The mode of operation is as follows: the feeding cylinder *a* is filled with pieces of wood charcoal or coke, of the size of a walnut, which are mixed with a certain proportion of dried potassa and filings or oxide of iron. The cover *b* is put on, and the damper *e* is made to slide by means of the rack and pinion, so that the charge put in *a* falls into the retort *h*. The diameters of the cylinders *a*, *h*, and *m* increase successively in size, and the substances acquire a conical shape, which is advantageous to the regular flow of gases and prevents the obstruction of the grates.

The nitrogenized gases come into the retort by the gas pipes. The formation of the potassium takes place only in that portion of the retort which is surrounded by fire; but, as by its volatility this metal rises upwards. it meets its nitrogen gas and is transformed into cyanide of potassium. These dispositions aid the chemical action, and there is no loss of potassium by volatilization. The remainder of the gases escape through the lower grate and flue, but not before they have passed through a mass of materials sufficient to transform the whole of the nitrogen into cyanogen. If the materials contained in the retort are in a pulverulent state, the flow of the gases may be aided by an exhauster, similar to those used in gas works.

When the operation has been continued long enough for the production of a certain quantity of cyanide of potassium, the sliding damper *o* is opened, and a portion of the product is made to fall into the receiver *q*. A fresh charge is then put into *a*, and the operation continues in the manner already explained.

The apparatus may be modified for distilling nitrogenized substances, by removing the lower grate and flue.

The advantages of this apparatus are:—

1. An economy of fuel, because a portion of the heat generally lost is here used.

2. A saving of potassa or its combinations, because the special disposition of the apparatus prevents its volatilization.

3. A saving of nitrogenized substances, on account of the large surfaces presented by the reacting substances, and because the reaction takes place in closed vessels.

4. An increased yield, resulting from the above causes, and because the products are protected from the contact of the air, until they are sufficiently cold, and until there is no longer any danger of the cyanogen being transformed into cyanic acid. Moreover,

the cyanogen gas is free from all compounds of sulphur and phosphorus.

5. A saving of labor, since the operation is continuous, and is effected with mechanical appliances.

5th. *Determination of the Value of the Fused Materials.*

It is an old complaint, says Mr. Brunnquell, that the manufacture of ferrocyanide of potassium is so backward, notwithstanding the progress of chemistry applied to the arts. Indeed, in the best managed works, the yield is only one-third of what it should be, and the remainder of the materials are entirely destroyed or valueless. Moreover, few of the recent processes have been adopted; and the manufacture by the nitrogen of the air, experimented upon in France and in England, has been abandoned. It appears, therefore, that the old process is still generally practised, and manufacturers should endeavor to work it to the best advantage. It is highly important to determine the truth relative to certain questions, which have often been put forward, but never settled in a satisfactory way; for instance, whether it is preferable to employ carbonized, or simply dried animal substances; whether the potassa should be previously mixed with the animal matters, or the latter added only when the potassa is melted; whether the fusion should be rapid and effected under a high temperature, or slow and at a low temperature, etc. There remain also to be decided whether purified potassa is preferable; whether the greater yield obtained in closed vessels is not more than counterbalanced by the greater cheapness of the open apparatus, and the greater facility of working, etc. Lastly, we should determine the best proportions between the potassa and the other materials. As an example of the doubt still left on these points, we shall give a few receipts.

1. MM. Hœfflmayer and Prückner, in 1837, gave the following proportions :—

100	kilogrammes of	blood	for	28 to 30	kilogrammes of	potassa.
100	“	horn	“	33 to 35	“	“
100	“	leather	“	45 to 48	“	“

That is to say, the less potassa, as the substances are richer in nitrogen, while it should be the opposite.

2. Mr. Gentele, in 1837, also gave certain proportions (*Technologiste*, vol. xii. p. 240) :—

For	65	kilogs. of	bone black . . .	100	kilogs. of	potassa	at 50°.
“	100	“	raw animal matters	100	“	“	“

We see, therefore, how variable are the “hard facts” presented by practical men.

3. An English periodical, the *London Journal of Arts*, of July, 1852, recommends from 15 to 20 kilogrammes of potassa for 100 kilogrammes of animal substances. With such a proportion of animal substances, it will be impossible to produce a fusion, and the experiments of Mr. Schinz prove that 100 kilogrammes of potassa will fuse at most from 130 to 140 kilogrammes of animal matters.

If, in a general way, and as Mr. Fleck advises, an average proportion of equal parts of potassa and animal substances be adopted, we should nevertheless modify the ratio with the nature of the substances employed, as their yield in nitrogen is quite variable.

Satisfactory answers to the important questions here mentioned cannot be made except after a great many experiments. The analytical chemist has not generally occasion to handle the fused materials, and the manufacturer possesses no rapid process for determining the composition of each fused batch, in order to be enabled to undertake a series of experiments without stopping the manufacturing operations, and without being obliged to arrive at the yield of each batch by a separate crystallization.

The following process gives results which are more than sufficiently accurate for practical use. It does not require much time, or a great chemical knowledge. Moreover, as manufacturing chemists possess no accurate way of testing the ferrocyanides, this method will be of some interest to them.

This method is based upon the precipitation of the ferrocyanide of potassium held in an acid solution of a sample from the fused mass, by a titrated solution of iron. There were two difficulties to overcome. The first was the determination of the exact point of saturation, which is not readily ascertained on account of the property possessed by Prussian blue of remaining suspended for a long time in the liquor. The second was the known property of Prussian blue, of carrying down with it a certain proportion of ferrocyanide of potassium. The first difficulty was overcome by a peculiar mode of operation, which is of general interest, inasmuch as it seems to open a new field in volumetric analysis, especially when there are intensely colored precipitates. A drop of the liquor, colored by a precipitate, is deposited upon a piece of unsized paper. The precipitate remains where it has touched the paper, but the liquor spreads itself around, and forms a colorless ring, which, by means of a proper reagent, may be made to assume a characteristic coloration. In our special case, a blue color is obtained with an iron solution before the saturation, and with a solution of ferrocyanide after saturation.

The point where the first reaction ceases, and where the second begins, is within the limits of two to four drops, and the accuracy of the test is within $\frac{1}{4}$ to $\frac{1}{2}$ of 1 per cent., which is quite sufficient in practice.

The second difficulty is overcome by direct experiment, and two or three tests agreeing together will show that the proportion of precipitated ferrocyanide of potassium is one-twentieth of the quantity present. The sulphocyanide of potassium present in the fused substances is no impediment to the analysis, because no sulphocyanide of iron is formed until all the ferrocyanide of potassium is precipitated. We have said enough for experienced chemists; however, we advise the employment of a moderately concentrated solution of a salt of peroxide of iron. The iron, held in the solution occupying 100 divisions of a graduated burette, is carefully determined after its precipitation with ammonia. The weight found will be used for determining that of the sample to be taken, in order that each division of the burette be equal to 1 per cent. of ferrocyanide of potassium.

The formula is—

$$1 : 2.257 + \frac{2.257}{20} :: n : x,$$

in which n is the quantity of oxide of iron found in 100 volumes of the titrated liquor, and x the weight of the raw fused mass to be employed for the test. As the fused mass is very hygroscopic and difficult to grind, it is advisable to take a certain weight of it, and reduce by calculus the number of divisions of the titrated liquor or percentage to the weight x. For instance, if 8.98 grammes of sample show 12.5 divisions, or 12.5 per cent., x grammes will give y per cent.

Preparation of the titrated liquor.—A pure sulphate of iron, without copper or excess of base, is prepared as follows: Dissolve in boiling water 250 grammes of sulphate of iron, and add a small quantity of sulphuric acid and a few clean scraps of iron. Let it stand until the liquor is clear and of a pure green color, then filter it rapidly, and allow it to cool in a covered vessel. After the crystals have been dried in several successive sheets of unsized paper, 83.28 grammes of them are weighed and dissolved in about 750 grammes of water. The solution is heated in a porcelain dish, and nitric acid is added several times, until red vapors cease to be disengaged. The liquor is then, together with the washings of the dish, poured into a vessel holding 1 litre, and when it is cold, sufficient pure water is added to make up the capacity of a litre. 100 cubic centimetres of this titrated liquor will precipitate 10 grammes of pure ferrocyanide of potassium. Therefore, every cubic centimetre poured out will correspond to 1 per cent.

Analytical operation.—Different portions of the fused substances are ground together, and 10 grammes weighed. This is dissolved in warm water, the solution is filtered, and the residue is washed several times with warm water. A few drops of the titrated liquor are then added, which produce a brown and blue precipitate. To neutralize the free alkali of the solution, hydrochloric acid is then poured in, the more slowly as the brown precipitate gradually disappears, and the blue one becomes more apparent. No account is taken of the gelatinous silica which is separated. Then four or five drops of the titrated liquor are poured in, and a drop of the blue liquor is deposited by means of a glass rod upon a piece of unsized paper. The colorless ring formed around the blue precipitate is touched with another rod wet with a solution of a salt of peroxide of iron, and if a blue color appears, the operation is continued as before. When the ring becomes brown-red, from the presence of sulphocyanide, the test is made with a solution of ferrocyanide, until a blue again appears. We should remark: First, that the coloration takes place only after a certain length of time; second, that it appears, in the majority of cases, in the middle of the border, and not at the extreme edge. In order to see how accurate this test is, the liquor is filtered at the end of the operation, and an addition of ferrocyanide will give a very pale blue coloration, if any.

The manufacturer should also note, before the test is made, the total weight of the fused mass, which weight may often vary from unknown causes.

6th. *Preparation of Prussian Blue by the Stephens Process.*

The invention comprises:—

1. Several improvements in the manufacture of the ferrocyanides of potassium and sodium.

2. A process for rendering Prussian blue soluble, and therefore better adapted for dyeing, printing, and writing.

We shall describe these two improvements successively, in the order presented by the inventor.

First improvement.—This consists in collecting the gaseous products, which, in the ordinary preparation of ferrocyanides with animal substances, are lost in the air, and in converting them into the ferrocyanide of sodium or of potassium. There is, therefore, a greater yield of the ferrocyanides.

The apparatuses necessary for these operations are simple enough to be explained in writing, without having recourse to drawings. These apparatuses are:—

1. An iron retort filled with alkali and animal matters, or any other substance holding nitrogen and producing ammonia. This retort should be brought to a dark read heat. It is provided with a cover, which is carefully luted on during the operation.

2. Another retort similar to the preceding one.

3. An hermetically closed vessel, of a cylindrical, or any other convenient, shape. It is charged with an alkali, and should be maintained at a red heat during the whole operation.

4. A closed vessel, holding an alkaline lye, and provided, for the escape of gases, with a pipe similar to a lamp burner.

5. A pipe connecting the retort with the cylinder, and delivering into the latter vessel the gases resulting from the carbonization of the animal substances in the retort.

6. A tube delivering the gases from the retort into the vessel holding the caustic lye. It is already understood that the retort and the cylinder are placed in furnaces, the fire of which is regulated by appropriate dampers.

Everything being arranged in the aforesaid manner, the gases produced in the carbonizing retort pass into the cylinder holding fused potassa (or soda), and form there a certain quantity of ferrocyanide of potassium (or of sodium). The portion of the gases which has not combined with the alkali, escapes through the tube into the closed vessel, and there forms another combination with the alkaline lye. Lastly, the uncombined gas escapes through the burner. The state of the operation is watched by burning the gas, and when the flame becomes small and weak, the communication between the retort and the cylinder is interrupted. The second retort, which has been charged with fresh substances, is then connected with the cylinder, and the operation proceeds as before.

When the gaseous products of a certain number of charges have traversed the cylinder charged with alkali, it is opened, and its contents, consisting of more or less ferrocyanide of potassium or of sodium, are poured into a closed iron vessel where they cool off. They are then lixiviated with pure water, in the ordinary way.

The decomposition of the carbonized animal substances may be completed in the same retort, by increasing the fire, and stirring the contents. During that time, the carbonization goes on in the other retort, at a lower temperature.

A similar effect, that is, the absorption of the gaseous products, may be obtained by placing in a conical iron chimney, with a grate at the bottom, dry potassa or soda, and passing the gases through it. This chimney, with its contents, may be removed when the flame becomes weak. The alkali is used for several operations, and is then treated in the ordinary manner for the extraction of the ferrocyanide of potassium or sodium.

Second improvement.—This consists in submitting the Prussian blue to a treatment, by which it becomes more easily soluble. The Prussian blue resulting from the combination of ferrocyanide of potassium, and of an iron salt, or the ordinary commercial article, is put into an earthenware pot, and just covered with some concentrated acid.

We may employ hydrochloric, or sulphuric, or any other acid, having sufficient action upon the iron; nevertheless, hydrochloric acid is to be preferred. If, however, sulphuric acid be used, it should be diluted with an equal volume of water, when the paste of blue and acid begins to turn white.

The Prussian blue should remain in the acid from 24 to 48 hours, or even longer. The mixture is then well stirred in a large quantity of water, in order to remove the iron salts. After settling, the liquid is siphoned off. A new quantity of water is then added, and the operation is continued until all of the acid and soluble iron salts are removed. When the washing is complete, a few drops of a solution of ferrocyanide of potassium produce no precipitate in the liquors. The blue is then drained upon a filter.

The Prussian blue, thus prepared, contains less iron than the ordinary commercial article. It is this modification which renders it more easily soluble. The drained product may be slowly dried in a stove room.

After this preparation, the blue is thoroughly mixed with oxalic acid, and pure water is added by small portions at a time, in quantity variable with the greater or less degree of concentration desired. The proportion of oxalic acid varies also with that of the water added.

It will be ascertained by trial that Prussian blue, which has been macerated in the aforesaid manner, will require for its solution a much smaller proportion of oxalic acid.

One part of oxalic acid will dissolve six parts of Prussian blue, weighed before maceration in hydrochloric or sulphuric acid. These proportions are sufficient for a concentrated solution; but more oxalic acid will be needed for a more dilute solution.

A Prussian blue, which has not been macerated in the strong acids, will require from two to three times its weight of oxalic acid, and yet, there will be a tendency to precipitation in the solution.

The principal obstacle to the employment of this fine color for dyeing, printing, and writing resulted from its supposed insolubility; but the process which we have just indicated, and which produces an entirely soluble Prussian blue, renders it applicable to the dyeing and printing of every cloth and substance which may be dyed and printed.

The process indicated above is not the only one known for rendering Prussian blue soluble. An aqueous solution of this color may also be obtained by precipitating the nitrate or sulphate of sesquioxide of iron, and possibly the perchloride, with a great excess of ferrocyanide of potassium. The precipitate is very soluble in pure water, but insoluble in water holding chloride of sodium or various other salts. This property allows of the separation of the precipitate.

7th. *English Process for the Manufacture of Prussian Blue.*

The following process, usually employed in England, gives a Prussian blue quite as fine as that of Berlin, and has a great analogy with the method actually practised in France.

Ox blood, mixed with oxide of iron, is dried in a reverberatory furnace, the bed and sides of which, to a height of about twenty to twenty-five centimetres, are formed of cast-iron plates bolted together, and with the joints made tight by a clayish cement. During the operation, the mass is continually stirred with an iron bar. This furnace should have a high stack with a good draft, so as to carry away the vapors, which are singularly fetid. When the blood is perfectly dried, which is a tedious process, it is removed from the furnace and broken into fragments while it is still hot. The division will be more difficult if the blood be cold. In fine weather, its drying may be completed in the sun. When it is not immediately mixed with the alkali, the powdered blood should be kept in open vessels and in a cool and aerated place, otherwise it will ferment and produce a disagreeable smell, and becoming viscous, it will be difficult to mix with the alkali.

The "blood lye" or solution of crude ferrocyanide is advantageously prepared with soda, which is cheaper than potassa. The proportions are one part of dry soda to six parts of perfectly dried blood. The soda ash should be free from sulphides, and on that account it is preferable to use the crystals, which are completely dried.

The mixture of oxide of iron, blood, and alkali is calcined in a large cast-iron crucible or kettle, which is covered, without, however, entirely excluding the contact of the air. This imperfect closing of the vessel is for the purpose of diminishing the rapidity of the combustion.

The two operations of calcination, and desiccation of the blood, are conducted simultaneously, and with economy of fuel. The calcining vessel is placed on the forepart of the reverberatory furnace, near the fire-bridge, where the intensity of the fire is greatest. The drying of the blood takes place near the chimney.

The mixture to be calcined soon softens, takes fire, and sinks considerably. The cover of the vessel is then raised with a hook, and a new portion of materials is introduced, and so on, until the vessel is filled. After ten hours of calcination, the vapors cease to catch fire, and the animal substances are entirely charred. The temperature is then raised, so as to redden the metallic vessel. The alkaline charcoal enters into a sort of fusion, and sticks to the spatula with which it is stirred. After one hour more of red heat, the contents are removed with an iron ladle, and thrown into an iron vessel, which holds a volume of cold water about double that of the blood used. After boiling, the liquor is filtered through several thicknesses of cloth, and the residue is again boiled and filtered.

All of the liquors and washings are collected in large but shallow cisterns, and exposed to the air. They are stirred now and then, in order to decompose the sulphides. When the lye no longer gives a black precipitate with the acetate of lead, it is treated with two parts of alum, and one-half part of sulphate of iron, for each part of dry carbonate of soda employed. The sulphate of iron has been previously oxidized by its ebullition with a very small proportion of nitric acid, or by passing some chlorine through it. The same result may be obtained by calcining it in the air, at a very low temperature. The alum and sulphate of iron are dissolved only when they are going to be used. The mixture of the liquors is effected by pouring the solution of the sulphates into that of ferrocyanide, and stirring continually. The precipitate of Prussian blue is washed several times by decantation with pure water. The washing should be continued as long as the liquor precipitates by the addition of ammonia. The blue is collected upon cloths, which are folded and pressed when it has acquired a certain consistency. The drying is effected in the shade and in stove-rooms, the temperature of which latter should not be over 25° C.

When the blue is sold in paste for distemper painting, and the printing of paper hangings, it is evident that it ought not to be pressed.

As long as Prussian blue is pasty and wet, it preserves its pure color. But it seldom happens even after the best conducted drying in a well ventilated room, that the blue fails to acquire a slightly green tinge, which defect is not seen in the fine Berlin blues. This defect is attributed to the production of a small quantity of ammonia, resulting from the decomposition of prussic acid.

The addition of a certain proportion of acid sulphate of potassa preserves the fine color of the Prussian blue, and admits of its employment with vegetable and essential oils. This salt results from the decomposition of nitrate of potassa by sulphuric acid, and is cheap, and easily found in the trade. It is probable that the acid sulphate of soda would have the same effect.

The expense of manufacture may be diminished by substituting for the alum a sulphate of alumina, which may be prepared on the spot, and does not require to be free from iron. This sulphate of alumina is prepared by making a stiff paste of clay and sulphuric acid, and moulding it into bricks, which are heated in a little space left at the end of the blood drying furnace. The liquor resulting from the lixiviation of these bricks is employed, directly and without evaporation, with the sulphate of iron and the solution of crude ferrocyanide.

An important condition, in the manufacture of Prussian blue, is to effect the calcination at the proper temperature. An excess of heat is injurious to the yield. In general, it is better to calcine longer and at a lower temperature.

A few manufacturers employ the crystallized ferrocyanide of potassium, with which they obtain the Prussian blue directly, and without the addition of acid. But it is easy to see that this process is not economical. The crystallized prussiate is obtained after saturation of the excess of alkali in the crude "blood lye." Subsequently, when mixing alumina with the Prussian blue, which contributes to its beauty and its velvety appearance, another alkali is employed for precipitating the alumina from the alum. There results therefore a double employment of chemicals, whereas, in the ordinary process, the excess of alkali in the raw solution of ferrocyanide decomposes the alum.

A manufacturer of Glasgow proposed to use the bone black which had been used for clarifying the sugar of refineries. This black, which was used only as manure, is again calcined with one-thirtieth part of alkali. The result is an abundant production of alkaline prussiate, without those disagreeable smells produced by blood and other uncalcined animal substances. The most interesting part of the process is, that the residue left after the lixiviation of the cyanides is a very energetic discolorizing substance, which is sold again to the sugar refiner. It appears that the same material may be used several times successively for clarifying sugars and producing cyanides.

§ 2. *Paris blue.*

Paris blue, also called *Turnbull's blue*, is a very handsome dark violet-blue pigment, in which the proportions of protocyanide and sesquicyanide do not appear to be in the same ratio as in the ordinary Prussian blue. It is said that its chemical formula is represented by 3 equivalents of protocyanide and 1 of sesquicyanide of iron.

Paris blue is prepared by different processes, the products of which are not always uniform in tone and in intensity of coloration. Generally, a green and pure protosulphate of iron is precipitated by the red prussiate of potash (ferricyanide of potassium), and the mode of operation is the same as with the ordinary Prussian blue.

The sulphate of iron may also be precipitated by a solution of raw ferrocyanide, and the excess of alkali removed by washings with pure water. The precipitate is then treated by hypochlorite of lime (bleaching powder) dissolved in cold water, and lastly, washed with dilute hydrochloric acid, and rinsed in pure water.

Paris blue is also produced by dissolving separately in 15 parts of water, 6 parts of sulphate of protoxide or of peroxide of iron, and six parts of yellow prussiate of potassa. The two liquors are mixed, and there are added to them one part of sulphuric acid, and twenty-four parts of concentrated hydrochloric acid. The whole is stirred, and, after standing a few hours, is treated by a filtered solution of hypochlorite of lime (bleaching powder) dissolved in eighty parts of water. This latter solution is poured by small quantities at a time, and stopped when there is an effervescence due to the disengagement of chlorine. The precipitate is then allowed to settle, and it is afterwards washed several times with pure water by decantation. After draining, it is moderately heated with dilute nitric acid, until it has acquired a fine dark blue color.

According to Mr. Raymond, a handsome quality of Paris blue is obtained by precipitating a nitrate of sesquioxide of iron with the yellow prussiate (ferrocyanide of potassium) or with "blood lye."

Mr. R. Warington, who has carefully studied the Turnbull blue, states that several efficient reagents may be employed in its preparation, that is, 1, the bichromate of potassa; 2, the chlorate of potassa; 3, a soluble persalt of iron; 4, a solution of hypochlorite of lime.

"When bichromate of potassa is used, only one-third of one equivalent should be taken, because this salt gives three equivalents of available oxygen. One equivalent of chlorate of potassa is sufficient for the oxidization, and sufficient hydrochloric acid should be added for decomposing the salt and setting its acid at liberty. Hypochlorite of lime (bleaching powder) is open to the objection of producing a quantity of sulphate of lime, when sulphate of iron or sulphuric acid is used. In the third case, when a persalt of iron is the oxidizing agent, the sulphate of peroxide is to be preferred. One equivalent of it is necessary for one equivalent of oxygen, and there is produced enough sulphuric acid to combine with the oxidized potassium after the iron has been reduced to the protoxide state.

"In the preparation of the sulphate of peroxide of iron, bichromate of potassa or chlorate of potassa is more advantageous than nitric acid, and there should be a sufficient proportion of sulphuric acid to dissolve the oxide of chromium produced. The decomposition of the chlorate of potassa should always be effected with hydrochloric acid. Since the protosulphate of iron absorbs one-half of one equivalent of oxygen to become sesquisulphate, it is evident that one-sixth of one equivalent of bichromate of potassa, or one-tenth of one equivalent of chlorate of potassa with the required proportion of acid, is sufficient for the transformation. When the oxidizing solution is prepared with the chlorate of potassa, this solution, after the oxidization of the white Prussian blue, may be precipitated by ferrocyanide of potassium for a new operation. If the bichromate of potassa be used, the protoxide of chromium will be precipitated to a certain extent by the ferrocyanide of potassium, and will contribute to the brightness of the color."

Mr. G. C. Habich, a chemist who has paid great attention to the manufacture of Paris blue, has proposed several valuable improvements, which render its preparation more certain and more economical.

"Among those coloring materials," says he, "which, from their numerous uses, require to be manufactured on a large scale, Prussian blue is certainly foremost.

"Its great qualities of body, and intensity of coloration, will always insure it a large sale; moreover, its mixture with chrome yellow produces a fine green cinnabar or leaf green (*Laubgrün*).

"The methods followed in certain works for the manufacture of this product, appear to me too expensive. Thus many persons still prefer the process by which the white precipitate, resulting from the decomposition of ferrocyanide of potassium by sulphate of iron, is rendered blue by means of sulphuric and nitric acids, although it is impossible to obtain with this product a good commercial green.

"I shall explain several processes by which the preparation of this product will be certain and economical.

"*First Process.*—This process is based upon the treatment of the white precipitate by the chlorine held in aqua regia.

"The precipitate of ferrocyanide of potassium (yellow prussiate) by the sulphate of protoxide of iron, is prepared in the ordinary manner; but the sulphate employed should be, as far as possible, free from oxide (basic sulphate). This result is arrived at by keeping in the acid solution of sulphate of iron, a small quantity of metallic iron, which, at the same time, precipitates the copper which may be present. Besides, it is desirable to operate the precipitation in the hot blood lye (crude prussiate of potassa), in order to avoid an absorption of oxygen, and a premature change of the precipitate to a blue color. Only the blue produced by the action of chlorine, nitric acid, etc., upon the white precipitate, possesses the intensity required in this pigment. That resulting from the oxidization by the air, even after all the hydrate of oxide of iron has been removed by hydrochloric acid, never produces a fine color, especially for the preparation of greens.

"In regard to the proportion of sulphate of iron, the general mistake is in employing too little of it. When ninety kilogrammes of sulphate of iron have been added to one hundred kilogrammes of ferrocyanide of potassium, a drop of iron solution in the filtered liquor produces no precipitate. However, the white precipitate has carried with it a certain proportion of ferrocyanide, which may be removed by washing. This proportion of a costly chemical is therefore lost, and in order to avoid its waste, we propose the following mode of operation. The iron solution is poured into that of ferrocyanide, which is stirred all the time, until precipitation no longer takes place, then one volume of the same iron solution, equal to one-ninth of that already poured in, is added. If we continue the stirring for about fifteen minutes, we may be sure that the whole of the ferrocyanide carried down by the precipitate is decomposed. We have, therefore, reached the degree of economy which may be expected at this period of the manufacture.

"The precipitate which has been left to drain until it has become a thick magma, is then peroxidized (blued) with a mixture of nitric and hydrochloric acids, prepared several days beforehand. The proportions naturally depend upon the degree of concentration of these acids, which is ascertained by means of a good hydrometer, and of corresponding tables found in treatises on chemistry. The mixture is so made that there are in weight 54 parts of anhydrous nitric acid and 36.5 parts of anhydrous hydrochloric acid. The proportion of aqua regia necessary for turning to blue the white precipitate, is 10.7 parts of anhydrous nitric acid (in the mixture) for 100 parts of ferrocyanide of potassium employed for the precipitation. Let us suppose that the nitric acid marks 30° Bé. (sp. gr. = 1.256 according to Graham), and the hydrochloric acid 23° Bé. (sp. gr. = 1.185); the first of these acids, according to the tables of Dr. Ure, contains 35.4 per cent. of anhydrous nitric acid, and the second 37.25 per cent. of anhydrous hydrochloric acid. From the preceding data, the aqua regia mixture will be 100 kilogrammes of the commercial nitric acid (holding 35.4 kilogrammes of anhydrous acid), and 62.2 kilogrammes of the commercial hydrochloric acid (holding 23.9 kilogrammes of anhydrous acid). Lastly, 40 kilogrammes of this mixture will be sufficient for bluing the precipitate resulting from 100 kilogrammes of ferrocyanide of potassium.

"The aqua regia is added by small portions at a time to the white precipitate, which is placed in a wooden tub, and is stirred all the while. It now remains to ascertain whether too much acid has been added, or if the intensity of the color may still be raised by a fresh addition of acid. Such defects may result from an improper preparation of the aqua regia.

"A small quantity of the blue color is put into a glass, and a drop of aqua regia is mixed with it. Then a blue mark is made with that sample of color upon a piece of paper, and is compared with a similar mark made with the stuff in the tub. If this addition of acid has increased the intensity of the blue, too little aqua regia has been employed, and more should be poured in. On the other hand, if the test sample has become slightly greenish, the proportion of the acids has been sufficient or too considerable. In order to decide this point, a new sample from the tub is put into a test glass, and a very small quantity of white precipitate is added to it. Should the color become more intense, we have the proof that too much acid has been added. This defect is remedied by adding by degrees a certain proportion of the white precipitate, of which there should always be a certain stock on hand, which is preserved in well-closed glass or stoneware jars.

"The washings and the other operations are then effected in the ordinary manner.

"*Second Process.*—The white precipitate of ferrocyanide of potassium by sulphate of iron, is rendered blue by a solution of perchloride of iron, which is reduced to the state of protochloride and may be used for another precipitation, instead of sulphate of iron.

"This perchloride of iron is made with iron ore, free from clay and carbonate of lime, and which may be brown or red hematite. If such an ore cannot be had, then the residue of the manufacture of sulphate of iron, known under the names of *caput mortuum*, colcotar and English rouge, may be employed. The oxide of iron, whatever its origin, is finely ground, and then treated in a lead tank with the crude hydrochloric acid of the soda works, which generally contains a certain proportion of iron. The mixture is frequently stirred for several days, and when the liquor is saturated with iron, it is decanted into another vessel, where it becomes entirely clear. It is this solution of perchloride of iron, which is used for bluing.

"The white precipitate is prepared in the manner already described, and drained. The magma is rapidly heated to the boiling point in a copper vessel, and then poured into a tub and stirred with the solution of perchloride of iron, which is admitted until the color has acquired its greatest intensity. In this operation, it is not necessary to watch the bluing with the same attention as when the aqua regia is used, because an excess of perchloride does not alter the purity of the color. This perchloride of iron is therefore added to a slight excess, that is, until a filtered sample of the liquor is turned decidedly blue by a few drops of a solution of ferrocyanide of potassium. When this point is reached, the liquor is filtered out (if it be desired to save nearly all of it), or the precipitate is left to settle, and the clear portion is decanted.

"This liquor, as we have said, is a solution mostly of protochloride of iron. It is poured upon old scrap iron, and may be used instead of sulphate of iron for a precipitation with ferrocyanide of potassium. This saving is one advantage of this method.

"The color is washed, etc., in the ordinary manner.

"*Third Process.*—In this method, the white precipitate is rendered blue by a solution of perchloride of manganese. The economy of the process depends on local circumstances, and on this account, it is necessary to state that the price of manganese ore is based upon its yield in binoxide, and that the less oxidized ores generally mixed with it may be dissolved in cold hydrochloric acid. Therefore, by treating an ordinary ore by hydrochloric acid, the value of the ore becomes enhanced, and there is obtained at the same time a very good reagent for bluing the white precipitate.

"The mode of operation is exactly the same as with the perchloride of iron. As the solution of protochloride of manganese, resulting from the bluing treatment, is without particular value to the manufacturer, we should avoid adding an excess of perchloride. Therefore, samples of blue are frequently taken, and their intensity compared. This is the only test practicable, by reason of the easy decomposition of the perchloride of manganese. The remaining manipulations are as usual.

"The residues of the manganese ores, after their treatment by hydrochloric acid, are carefully washed and dried before being sold as peroxide or purified manganese.

"*Fourth Process.*—A solution of chromic acid is also an excellent reagent for bluing the white precipitate of ferrocyanide of potassium by sulphate of iron. The only disadvantage of the method is, that the resulting salt of oxide of chromium is difficult to place on the market.

"The following is the mode of operation: 10 parts of bichromate of potassa are dissolved in 100 parts of hot water, and when the solution is cold, 13.5 parts of concentrated sulphuric acid are added to it. The mixture is kept in closed glass vessels.

"The white precipitate, prepared as usual, and in the form of a magma, is heated to the boiling point. The chromic liquor is then added, until the maximum of intensity in the liquor is reached.

"Before closing these remarks on Prussian blue, I shall again point out the mistake made by certain manufacturers who prepare the blue with the intention of producing greens by an admixture of chrome yellow, and who believe that their mode of operation is perfect, whereas it is wrong. I am acquainted with manufacturers who neglect all the precautions we have mentioned, and who allow the white precipitate of ferrocyanide of potassium by sulphate of iron to become blue by the contact of atmospheric air. They certainly ignore the fact, that by their process they lose a notable proportion of the ferrocyanide, which is the most expensive material of the manufacture. It has been established by accurate chemical experiments, that 50 per cent.* of the ferrocyanide employed in the precipitation of a salt of protoxide of iron, is carried down with the white precipitate, and that during the bluing, the greater part of this ferrocyanide is dissolved and washed away. This loss is prevented or greatly diminished when one of the above processes is followed in bluing. When it is desired to avoid ony waste, the liquor decanted or filtered from the white precipitate should be collected in a special tank, and precipitated by a solution of sulphate of iron."

§ 3. *Monthiers' blue.*

Mr. Monthiers has discovered that Prussian blue will combine with ammonia, and that the resulting color is finer and more durable than the ordinary article. The mode of operation is as follows:—

Pure hydrochloric acid is saturated with iron, and the resulting solution of protochloride of iron is mixed with an excess of aqua ammonia. The liquor is filtered, and the filtrate is received in a solution of ferrocyanide of potassium. The resulting white precipitate is collected upon a filter, and left exposed to the contact of the air, when it soon becomes blue. It is then washed with a solution of tartrate of ammonia, in which it is not soluble like the ordinary blue, in order to dissolve any excess of oxide of iron held in it. The washing is continued until nothing more is dissolved, when the article is dried at a low temperature.

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* More likely 5 per cent. See p. 233.—Trans.

§ 4. *Testing the value of Prussian blue, and its adulterations.*

There are in the market, under different names, many coloring substances having Prussian blue for a basis, and which often contain quite a large proportion of some white substance. The common sorts of greens for house painting are mixtures of Prussian blue, chrome yellow, or some other organic yellow, with a greater or less proportion of white material. As Prussian blue may easily be transformed into ferrocyanide of potassium, Mr. Brunnquell thinks that the method which has already been explained for testing the crude ferrocyanide, may be applied to the analysis of Prussian blue and its mixtures.

The operation is as follows: Boil 6.79 grammes of the color to be tested with a solution of caustic potassa until all the blue or green coloration has disappeared; then filter, and wash the residue several times with hot water. The liquors are tested as has already been explained. In this case, as there is no sulphocyanide of potassium, the test is continued until there is no longer a blue coloration with the ferric solution. At this period of the operation the volume of this solution, which has been poured out, is noted, and a few more drops added, until the blue coloration reappears with a solution of ferrocyanide. One-half of the number of these drops is added to the volume previously noted, and the percentage of Prussian blue is obtained as accurately as may be done by a volumetric test. If the blue precipitate does not deposit well upon the paper, but runs towards the edges, some common salt, or other indifferent salt, is added to the tested solution. There is a Prussian blue which is soluble in pure water, but not in a solution of common salt.

There are several ways of testing the commercial white cyanide of potassium. Baron Liebig has given a process which seems as accurate as possible. Messrs. Fordos and Gélis have also published a method which does not appear so accurate, and which requires the employment of iodine, an expensive substance. As practical manufacturers are generally opposed to the preparation of test liquors, which require a certain degree of skill in manipulation, Mr. Brunnquell refers again to his method in case it be desired to avoid the expense necessitated by the Liebig process. The mode of operation is as follows:—

Dissolve 9.246 grammes of cyanide of potassium in a small quantity of water, and add about the same quantity of the solution of pure sulphate of iron. The whole is boiled for some time with a solution of potassa, and then filtered, and the residue washed. The liquors are treated in the manner explained in § 1 and § 2. Each degree (volume) of the titrated liquor corresponds to 1 per cent. of pure cyanide of potassium.

The substances generally employed for adulterating Prussian blue are: Alum, an excess of oxide of iron, starch, the carbonate and the sulphate of lime, alumina, and sulphate of baryta.

The alum, oxide of iron, and alumina are dissolved by digesting the blue in sulphuric acid, diluted with eight to ten times its weight of water. After filtering, an excess of ammonia is added to the liquor, and there is produced an abundant reddish precipitate of alumina and oxide of iron. Caustic potassa will dissolve the alumina; the blue remains undissolved in the acid.

Starch is recognized by the eye, with or without the aid of a microscope. But the best test consists in boiling the Prussian blue in water, and filtering it. A drop of iodine solution in the cold filtrate produces with starch an intense blue coloration.

Each time that a Prussian blue, stirred in pure water, effervesces by the addition of an acid, it is a proof that it is mixed with a carbonate, and if the filtered liquor, rendered neutral, gives a white precipitate with oxalate of ammonia, carbonate of lime is the adulterant.

Plaster of Paris (sulphate of lime) is detected by boiling the sample of Prussian blue in water slightly acidulated with nitric acid. The liquor is filtered, and the blue remains upon the filter. A few drops of a solution of chloride of barium, added to the filtrate, will produce a white precipitate of sulphate of baryta.

We have already seen that Prussian blue is rendered soluble after a treatment with hydrochloric and oxalic acids; therefore, if, after a sample has been rendered soluble, there remains upon the filter a white substance, insoluble in water and acids, we conclude that this blue has been adulterated with sulphate of baryta.

§ 5. *Mineral blue, Antwerp blue.*

Mineral or Antwerp blue is a mixture, in variable proportions, of Prussian blue, alumina, magnesia, and oxide of zinc. Its color varies from a light to a dark blue, and it is employed for oil and distemper painting, and especially for paper hangings.

It is prepared like Prussian blue, with this difference, that the sulphates of magnesia and zinc, and the alum, are added to the lye of crude ferrocyanide of potassium. The remainder of the operation is as usual.

The name of "mineral blue" is sometimes given to white earths (kaolins, etc.), colored with indigo and hydrated oxide of copper. A small quantity of Nordhausen sulphuric acid decomposes Prussian blue, and dissolves indigo without changing its color. A few drops of ammonia, poured into the liquor, will produce an intense blue coloration if copper be present.

§ 6. *Thénard blue, or cobalt blue* (*subphosphate of cobalt*).

The discovery of this fine color is due to the chemist Thénard. This blue is a basic phosphate of cobalt, which, being calcined with alumina, gives a pigment sufficiently handsome to replace ultramarine blue, which is more expensive. Cobalt blue could be advantageously substituted for ultramarine, even for delicate paintings, except for one single defect, pointed out by Mr. Bourgeois, it has a violet hue under artificial light, and this naturally defeats the colored combinations of the artist.

Cobalt blue acquires all its intensity of coloration only after exposure to the air. Messrs. Bourgeois and Colomb have succeeded in giving it sufficient body; and, although not so pure in color as ultramarine, it produces, with silver white, different tones. It should always be remembered that the tones produced with cobalt blue will become more intense after a long exposure to the air, and that they acquire a slightly greenish tinge, which is not the case with ultramarine.

The preparation of cobalt blue, according to Thénard, is as follows: The roasted cobalt ore from Tunaberg, Sweden, is heated with an excess of dilute nitric acid, and the solution is evaporated nearly to dryness in a porcelain or platinum dish. The residue is boiled with water, and filtered, in order to separate a deposit of arseniate of iron. A solution of basic phosphate of soda is then poured into the filtrate, and there is produced a precipitate of basic phosphate of cobalt, which is violet, but may become of a pink color by remaining under water.

This precipitate is washed and collected upon a filter. While it is still gelatinous, one part of it is *thoroughly* mixed with eight parts of hydrated alumina, recently precipitated from a solution of potassa alum by ammonia. The mixture is first dried in a stove-room, or upon a furnace, until it is dry enough to be brittle. It is then calcined at a cherry-red heat for half an hour, in a covered clay crucible. The resulting blue color is kept in glass jars.

The operation will always be successful, if the alumina has been prepared with a sufficient excess of ammonia, and if it has been washed several times with very clear water.

In this preparation of cobalt blue, the phosphate of cobalt may be replaced by the arseniate of cobalt. But, instead of one part of the violet precipitate of phosphate of cobalt, one-half part of the arseniate will be sufficient for eight parts of gelatinous alumina. The arseniate of cobalt can be obtained by precipitating the solution of cobalt with one of arseniate of potassa.

As the gelatinous alumina, necessary for the manufacture of cobalt blue, enters into the preparation of several other colors, we shall here explain its preparation. The alum is dissolved in a quantity of water, at least three times that strictly necessary for the solution, and is then precipitated by an excess of ammonia. After stirring, the precipitate is left to settle, and the liquor is decanted with a siphon. Several washings are made with pure water, and the liquors are decanted or siphoned off. Lastly, the residue of gelatinous alumina is collected upon a filter.

Cobalt blue, mixed with whites, gives light blue tones, with a slightly violet tinge. It is very durable, becomes more intensely colored in the air, and resists the action of fire, acids, and alkalies.

The beauty, or rather the intensity, of Thénard blue, depends on the proportions of alumina added. With equal parts of phosphate of cobalt and of hydrated alumina, the blue is greenish; with four to five parts of alumina to one of phosphate, the blue is pure. Intermediate tones and hues will be obtained by varying the proportions.

Several modifications have been introduced in the manufacture of cobalt blue, the most important of which is that of Mr. Binder, described in the *Technologiste*, v. 5, page 55.

"I dissolve 6 kilogrammes of alum, free from iron, in a vessel of lead or earthenware, and filter the boiling solution into a wooden tub, 1.7 metre high and 1 metre in diameter, one-third filled with pure water. I then precipitate the alumina with a solution of potassa; the tub is filled with water, and, after settling and decantation of the clear liquor, I add a new quantity of water, and so on, until the washings no longer precipitate by the chloride of barium.

"I dissolve 500 grammes of sesquioxide of cobalt in 1500 grammes of hydrochloric acid at 22° Bé., and evaporate the solution to dryness. The residue is again dissolved in 3 kilogrammes of hydrochloric acid, and a stream of sulphuretted hydrogen is passed through it, in order to separate the foreign metals which may be present. I filter, evaporate again to dryness, and dissolve the residue in enough water to obtain from 4.5 to 5 kilogrammes of solution.

"When these two preliminary operations are completed, I precipitate 3, 4, 5, or 6 kilogrammes of the cobalt solution (according to the intensity of coloration desired) with ammonia. A too great excess of this reagent is to be avoided, because it may redissolve the cobalt. After the precipitate has been thoroughly washed, I pour it into the water which holds the divided alumina in suspension. The mixture should be constantly stirred for at least half an hour, in order to have a perfect mixture of the two precipitates.

"If the supernatant liquid be of a reddish hue, it is a proof that a small proportion of cobalt has been dissolved. A little ammonia is then added, and the precipitate is allowed to settle. After decantation, a new quantity of water is added, and so on, several times. The precipitate is collected in a fine cloth bag, drained, pressed, and dried in a stove-room. Lastly, it is calcined at a red heat for two or two and one-half hours, in clay crucibles.

"After cooling, the color is finely ground in a mill, dried, ground again upon a slab, and sifted. 6 kilogrammes of the cobalt solution give the finest color, and 3 kilogrammes the clearest."

It has also been proposed to replace alumina by lime, in the manufacture of cobalt blue. Mr. Boullai-Marillac, the inventor of the process by which the color obtained is a phosphate of lime and of oxide of cobalt, claims that the product is richer and more velvety in appearance than the Thénard blue.

§ 7. *Blue hydrated oxide of copper. Péligot blue.*

The hydrated oxide of copper, precipitated from the solution of a copper salt, by an excess of potassa or soda, becomes black rapidly, even if the washing be effected with cold water. Mr. Péligot, in 1858, succeeded in obtaining a blue hydrated oxide of copper, which resists boiling water, and may be heated at 100° C., without being altered. It is true that it retains traces of ammonia, but the proportion is no greater than that of the foreign matters always found in precipitated oxides.

Mr. Péligot prepares his blue with all the soluble salts of copper, the sulphate being preferred. A very dilute solution of the copper salt is treated with an excess of ammonia, and then precipitated by potassa or soda. Instead of aqua ammonia, an ammoniacal salt may be employed. The same color is also produced by adding a large quantity of water to a slightly ammoniacal solution of nitrate of copper.

The color is not so deep as that of English blue ashes, but it is purer.

Concentrated aqua ammonia dissolves from seven to eight per cent. of this hydrate, and this liquor is the best dissolvent for cellulose and other substances more or less soluble in the reagent of Mr. Schweitzer, that is, an ammoniacal solution of oxide of copper.

§ 8. *Blue of manganate of lime.*

Mr. Kuhlmann made, in 1841, a series of experiments for extracting potassa from feldspar in an economical way. The best results were obtained by melting powdered feldspar with chloride of calcium. It was possible to extract, by this method, twenty parts of chloride of potassium from certain kinds of feldspar.

While trying economical processes for the preparation of the chloride of calcium, Mr. Kuhlmann calcined in large furnaces a mixture of chalk and of the residues of the manufacture of chlorine, which are composed of chloride of manganese and of a certain proportion of chloride of iron. The result of this calcination is a mass of chloride of calcium, colored green by a protoxide of manganese.

During the repairs made on a furnace, employed for six months in effecting these calcinations, Mr. Kuhlmann remarked that in the mass of chloride of calcium nearest the fireplace, and where the heat was the greatest and oxidizing, there were cavities filled with magnificent black crystals, whereas the superficial portions of the mass were of the brightest blue.

The black crystals are formed of a certain oxide of manganese, with 3.5 per cent. of oxide of iron, and their composition corresponds to the natural ore, called pseudo-morphic Hausmannite or acerdese.

Mr. Kuhlmann ascertained that the blue substance was a manganate of lime, which, on account of its magnificent coloration, should attract the attention of chemists. All the attempts made up to the present day, by Messrs. Chevillot, Edwards, Forchhammer, and Fromherz, in order to prepare it, have been unsuccessful.

In the opinion of Mr. Kuhlmann, the formation of this manganate is probably due to the decomposition of the chloride of calcium by steam, and to a certain solution of the lime in the undecomposed chloride of calcium. Baron Liebig attributes the alkalinity of a solution of chloride of calcium, to the partial decomposition of the chloride in water. Mr. E. Krauss has stated that the decomposition is the greater, as the chloride has been oftener moistened with water and then calcined. Lastly, Mr. Pelouze has recently pointed out the rapid decomposition of chloride of calcium, under the influence of steam at a high temperature.

If the attempts for obtaining the manganate of lime have been unsuccessful, it is due, according to Mr. Kuhlmann, to the lime not being under so favorable conditions for acting upon the manganese oxide, as when it is in solution in the chloride of calcium.

A great solubility is not necessary to explain the reaction, because we may admit that once a portion of lime becomes transformed into manganate, another equal portion will dissolve in the chloride.

Such as it is accidentally produced in reverberatory furnaces, the manganate of lime is of an ultramarine blue and appears crystalline. It is insoluble in water, although not durable when in contact with it. Like all manganates, it is easily transformed into a permanganate under the influence of weak acids, and even of carbonic acid.

When the arts, Mr. Kuhlmann concludes, by appropriate proportions and apparatus, shall have succeeded in manufacturing a cheap manganate of lime, they will have become enriched with a most precious agent for discoloration and disinfection.

§ 9. *Indigo.*

It was only about the middle of the sixteenth century, that indigo was brought from India to Europe. This coloring substance is furnished by the leaves of several plants, called *Indigotifera*, on account of this property. The plants most generally employed for its preparation are—

1. *Indigotifera argentea*, or wild indigo. Its yield in indigo is less than that of the other plants, but in quality it is the best.

2. *Indigotifera tinctoria*, or French indigo. It produces the greatest proportion of color, but in regard to quality it comes the last.

3. *Indigotifera disperma* or *guatemala*. This plant grows higher and is more ligneous. The quality of its indigo is better than that of the preceding.

4. *Indigotifera anil* or *anil*. Its indigo is the least oxidized.

5. Lastly, the *polygonum tinctorium*, the cultivation of which is recommended in France, *the nerium tinctorium*, and many other plants.

The greater part of these plants are indigenous to India and Mexico, and have been introduced into the two continents of America, into China, Japan, Madagascar, Egypt, etc. They belong to the *Diadelphia decandria* of Linnæus, of the family of *Leguminous* plants. The indigo is extracted from these plants in the following manner: when the leaves have attained their maturity, they are collected, washed, cut, and placed in tanks with a certain proportion of water. They are kept down by means of boards loaded with stones. The fermentation soon begins, the liquor becomes green and acid, and a great number of bubbles and rainbow colored particles rise to the surface. The liquor is then run into a lower tank, where it is stirred, and the indigo is separated by the addition of a sufficient quantity of lime-water. The deposit is washed several times with water, and dried in the shade.

Pure indigo is firm, odorless, and tasteless, of a violet-blue color, unaltered in the air, insoluble in water and ether, and but slightly soluble in boiling alcohol, from which it separates by cooling. It is easily decolorized by chlorine, and according to certain experiments, by essence of turpentine. If it be heated in a retort, a portion is volatilized and condenses in the shape of copper-colored needles, while the remainder is decomposed. Weak acids do not dissolve it, but nitric acid transforms it into a yellow and bitter principle. It is easily dissolved by concentrated sulphuric acid. Cold hydrochloric acid does not react upon indigo, but, with the aid of heat, it acquires a yellow color, due to the decomposition of a small quantity of indigo.

Indigo loses its blue color by a protracted contact with deoxidizing substances. Deoxidized indigo is soluble in water, especially with the aid of alkalies. When kept in suspension in water, it is deoxidized by sulphuretted hydrogen, hydrosulphate of ammonia (sulphide of ammonium), protosulphate of iron (green copperas), potassa, and the protoxide of tin. In dyeing operations it is generally deoxidized with the following substances:—

Protosulphate of iron	2 parts.
Slaked lime	3 "
Finely powdered indigo	1 "
Water	150 "

All of these substances are put into a glass matrass, and are kept there for several hours at a temperature of 40° to 50° C. The lime forms with the sulphuric acid an insoluble sulphate of lime, and the protoxide of iron is precipitated as peroxide after having taken the oxygen from the indigo. The blue color is restored by an oxidation resulting from exposure to the air. The solution of indigo in sulphuric acid is deoxidized by iron filings or zinc.

Commercial indigo is never pure, and the pure article is obtained by sublimation in closed vessels, the sublimate being in needle-like crystals. The fracture of good indigo is smooth, and the portion rubbed with a finger-nail acquires a coppery lustre. The qualities generally preferred are light, and with a deep and bright-violet blue color.

There are in the trade at least sixty varieties of indigo, the better known of which are denominated by the names of the countries they come from, thus:—

1. *Indian indigo* is called *Bengal*, *Madras*, *Coromandel*, etc.

2. *Guatemala indigo*, *indigo flore;* this is the most esteemed of all.

According to Mr. Chevreul, commercial indigo is composed of—an immediate principle (indigotin), a red resin soluble in water, a greenish-red substance soluble in water, carbonate of lime, alumina, silica, and oxide of iron.

Berzelius has found in it—gluten, brown, red, and blue coloring principles, fecula, silica, alumina, oxide of iron, and lime.

According to Messrs. Dumas and le Royer, pure indigo is composed of—

Carbon	73.26
Nitrogen	13.75
Hydrogen	2.83
Oxygen	10.16
	100.00

Indigo is generally applied with size, because oil renders it black or green. It possesses less brightness than Prussian blue. Mixed with a white, the resulting blue is grayish, and the exterior becomes decolorized.

Indigo is sometimes adulterated with various substances. Prussian blue is detected with a caustic lye of potassa, the color of the sample losing part of its intensity. Pure indigo is not acted upon by this solution. Fuming sulphuric acid decolorizes Prussian blue, and dissolves the indigo without changing its color. Chlorine decolorizes indigo, and has no immediate action upon Prussian blue. Lastly, if the suspected sample be burned, and the ashes be treated with hydrochloric acid, the solution will give with ammonia and the ferrocyanide of potassium, characteristic tests of the presence of iron, should Prussian blue be present. The proportion and the appearance of the ashes give also good indications as to the quality of the indigo.

Indigo, on account of its high price, and of the indefinite color of its mixtures, is not employed by painters. It is used by manufacturers of paper hangings.

§ 10. *Blue carmine, indigo carmine, blue of England or Holland.*

Nordhausen sulphuric acid dissolves indigo almost entirely. In accordance with the proportions of acid held in it, this solution bears different names. Thus, *indigo purple* is formed of equal equivalents of acid and indigo; eight to ten parts of indigo, and sixteen to twenty of sulphuric acid, constitute *indigo carmine* or *sulphoindigotic acid.* Generally, painters mingle these two solutions under the names of *Saxony blue, blue in liquor*, and *composition blue.*

A blue carmine is sometimes employed in painting, which is obtained by precipitating Saxony blue or the blue in liquor by potassa. The operation is as follows:—

A frigorific mixture is made with common salt and broken ice, in which there is placed a vessel holding 4 kilogrammes of fuming sulphuric acid. 1 kilogramme of finely powdered indigo is then added to the acid, by small portions at a time, and stirred all the while. When the solution is complete, the clear liquor is decanted, and a solution of tartrate of potassa is added to it until precipitation no longer takes place. After settling and decanting, the precipitate is collected and washed with cold water until the washings cease to be acid. The color is then drained upon a filter, and dried in the dark. Blue carmine has a very bright bluish hue, which does not stand the action of light. It is employed, with size, in the manufacture of artificial flowers.

There is also a color, called *blue of England, blue of Holland*, and *platt of indigo*, which is fine enough, but wanting in durability. It is a mixture, in undetermined proportions, of Prussian blue, indigo, smalt, chalk, and starch, which is thickened and rendered homogeneous with a mucilage of rice flour, and dried in the shape of lumps or troches.

One of the reasons why indigo carmine is often sold in the pasty shape, is that it becomes covered with a white efflorescence, when it has been dried and kept for some time. This efflorescence is due to salts in the waters employed for washing, which salts are left purposely, in order to prevent a loss of carmine, which is soluble in pure water. However, the pasty state is objectionable on account of the greater difficulty and cost in transportation, and of the opportunity of adding an excess of water. By the experiments of Mr. J. J. Pohl, it is demonstrated that a small quantity of glycerin will prevent the efflorescence of indigo carmine, and will permit it to be kept for years without any deleterious effect upon the beauty of the product, or upon the colors it produces on tissues. An addition of 3 to 4 per cent of glycerin, calculated from the weight of dry carmine, is sufficient to arrive at that result, and the present low price of glycerin cannot be a bar to this mode of preservation.

§ 11. *Ultramarine blues.*

The coloring substance known under the name of ultramarine blue, has been the subject of a great number of chemical researches. The operations of the chemists have been of two kinds: first, analysis has been resorted to, in order to arrive at the composition of the native ultramarine; second, from the synthesis of the results obtained, there has resulted an artificial preparation of a similar compound.

Ist. *Real or Native Ultramarine Blue.*

Ultramarine is extracted from *lazulite*, *lapis lazuli*, or *azure blue lazulite*, a mineral which belongs to the granitic rocks. This substance, which is remarkable for its fine azure-blue color, is not altered even by a violent fire.

Ultramarine-lazulite is generally found in rolled and scattered lumps; the finest comes from Prussia, China, and the Great Bucharia. It is a dense and opaque stone, of a pure or dirty blue color, and gold spangles are scattered in the gangue. The ultramarine blue is separated from this stone by the following process, indicated by Thénard: The stone is disintegrated by being brought to a red heat, and then thrown into cold water; it is afterwards powdered and intimately mixed with twice its weight of a mastic, composed of resin, wax, and boiled linseed oil. The resulting paste is wrapped in a cloth, and kneaded in hot water several times, in order to express the color. The first water is generally dirty and thrown away; the second gives a blue of the first quality; the third a blue inferior to the former; the fourth water a still inferior product, and so on, until the product is so pale, that it is called *ultramarine ash*. These liquors are allowed to settle, and the different blues require but another finer grinding, effected with the greatest cleanliness, before they are dried. This operation is based upon the property of ultramarine blue, of being less adhering to the mastic than the foreign matters with which it is associated.

Thénard observes, that if, as is customary with certain color manufacturers, the hot red stone be thrown into vinegar, instead of water, the yield will be diminished, because the acid, although weak, attacks the color at a high temperature.

As ultramarine blue, on account of its variety, beauty, and durability, is exceedingly costly, and, according to Thénard, is sold at prices ranging from 80 to 200 francs per 30 grammes, it is not employed for ordinary painting.

It will be easy to ascertain whether ultramarine is mixed with cobalt blue, by digesting a pinch of the sample in nitric acid. After a little while, the ultramarine is entirely decolorized, while the cobalt retains its blue color.

It may also happen that ultramarine is adulterated by Prussian blue and indigo. The latter substance will be detected by placing a small quantity of the sample upon incandescent charcoal, and there is produced a bluish vapor, accompanied by the characteristic smell of burning indigo. If the sample be treated at a moderate temperature with ammonia, the Prussian blue is decomposed, but its color will reappear by pouring into the liquor a few drops of acid nitrate, persulphate, or perchloride of iron.

"The preparation of native ultramarine," says Mr. Brunner, "is effected mostly by mechanical processes, tending to separate it from the foreign matters. Although the methods may differ in certain particulars, they are all based upon a levigation (floating) of the powdered substance.

"When lazulite, after several calcinations, followed by immersions in cold water, has become sufficiently brittle, it is finely ground. This powder is combined with a fused mixture of wax, resin, pitch, and oil, and then worked with hot water in a stone mortar. The mineral gangue settles, while the ultramarine remains suspended in the liquid. By repeating this operation several times with the proper care, the blue colored substance is separated as completely as practicable, and it is sorted into different qualities, which are sold at different prices. The inferior quality, containing a certain proportion of gangue, is called ultramarine ash. The high price of the first quality, besides the cost of a long and tedious labor, is due especially to the small amount collected, that is, according to Clement and Desormes, from two to three per cent. of the best lazulite.

"We owe the first analysis of this substance to the two afore-named chemists, who have found in it—

Silica	35.8
Alumina	34.8
Soda	23.2
Sulphur	3.1
Carbonate of lime	3.1
	100.0

"Many years after, C. G. Gmelin made a new analysis of a sample of average quality, obtained from Paris. The composition was—

Silica	47.306
Alumina	22.000
Soda (with potassa)	12.063
Lime	1.546
Sulphuric acid	4.679
Sulphur	0.188
Water, resinous matter, and loss	12.218
	100.000

"I am not acquainted with other analyses of ultramarine, except those just indicated. On the other hand, several analytical researches have been made upon the lazulite itself, the mineral which furnishes this expensive color. Although it is impossible to draw rational conclusions from analyses made with different samples of such a complicated mineral, nevertheless the effort has been made to arrive by this process at some indications upon the nature of the coloring substance. Here are the results of these analyses :—

	Klaproth.	L. Gmelin.	Varrentrapp.
Silica	46.0	49	45.50
Alumina	14.5	11	31.76
Soda		8	9.09
Lime	17.5	16	3.52
Sulphur			0.95
Sulphuric acid	4.0	2	5.89
Oxide of iron	3.0	4	0.86 (metal)
Chlorine			0.42
Water	2.0		0.12
Carbonic acid	10.0		
Magnesia		2	

"The most important technical question was, to ascertain which were the elements composing the blue color. On this subject opinions differed.

"Margraff, who, as early as 1758, had published a few researches upon lazulite, combated the opinion, then general, that this mineral contained copper; but at the same time he thought that the color was due to iron.

"Guyton-Morveau believed that the coloring principle was a sulphide of iron, and many chemists were of the same opinion. Even more recently, Mr. Varrentrapp was of the same belief, although Clement & Desormes certified that not a trace of iron was found in a fine sample of ultramarine. But the latter chemists say nothing about the nature of the coloring material."

2d. *Artificial Ultramarine.*

A few accidental observations gave the idea of undertaking researches upon the artificial preparation of a substance similar to the coloring material of lazulite.

Thus Goethe, in his travels in Italy (Palermo, April 13th, 1787), mentions that in Sicily they use a certain vitreous substance formed in lime-kilns. It is sawed into slabs, which are used, instead of lapis lazuli, for the decoration of altars, mausolea, and other ornaments of religious temples.

Another observation, made by Tessart, in a French soda-works, gave more precise data upon the possibility of forming a blue combination, similar to ultramarine. This manufacturer had noticed that a substance of a fine blue color was formed in the soda furnace, when a certain kind of sandstone had been employed for its construction; but that the color disappeared when bricks were the building material. Vauquelin found in this blue compound, separated from about 44 per cent. of sand mechanically mixed, sulphate of lime, sulphate of soda, chloride of sodium, silica, alumina, and a small proportion of sulphur and iron; and, from this analysis, he demonstrated the analogy existing between this compound and the native ultramarine.

Therefore, there remained but to discover, by synthetical researches, a method by which such a compound could be reproduced, and the problem was resolved in France. Mr. Guimet was the first to put into the market a product nearly as fine as real ultramarine, and, at the present time, he still manufactures one of the finest known.

Savans and manufacturers worked the subject with great energy, and the latter, possibly in an empirical manner, but certainly after analytical researches, discovered several processes for preparing products which are now abundant in the trade. It is but natural that few precise data have been made known, because it is not customary for manufacturers to publish their processes. But it is certain that these processes are sure, and improved, if we judge from the fine qualities of ultramarine which are now in the market, and at very moderate prices.

Without any doubt, this manufacture has been greatly aided by the publication, in 1828, of a memoir of C. G. Gmelin, in which this chemist gives a precise formula for the preparation of artificial ultramarine. But, although it may be true that this formula is not to be trusted in every particular, or that it does not always furnish an identical product, or that it does not admit of its manufacture at the present low prices, it is but justice to assert that this memoir must have been the point of departure for all the researches made up to the present time.

More recently, Messrs. Elsner and Varrentrapp have published the analysis of two kinds of artificial ultramarine. Here are the results of their researches:—

	Varrentrapp.	Elsner.
Soda	21.476	33.00
Potassa	1.752	—
Lime	0.021	—
Alumina	23.304	20.50
Silica	45.604	40.00
Sulphuric acid	3.830	3.40
Sulphur	1.685	4.00
Iron	1.063	1.00 oxide.
Chlorine	Traces.	—

The formula given by Gmelin for the chemical preparation of ultramarine, may be condensed as follows:—

Gelatinous silica (prepared in the ordinary manner from a natural silicate) is dissolved in a solution of caustic soda, and pure hydrated alumina is added, until the proportions amount to thirty-five parts of anhydrous silica, and thirty of anhydrous alumina. The mixture is evaporated and brought, by stirring carefully, to the state of a dry powder, which is ground and thoroughly mixed with an equal weight of sublimed sulphur. There is added to this mixture another compound of equal parts of carbonate of soda and sublimed sulphur, equal in weight to that of the dry silico-aluminous powder. The whole is then introduced into a closed crucible, and kept for two hours at a strong red heat. The greenish mass thus obtained is again heated either in crucibles or in clay tubes, but without the access of the air, until it has acquired the desired blue color. Gmelin thinks that this last operation is the most difficult, and he describes several modes of operation for arriving at a satisfactory result.

Lastly, Gmelin suggests, that in manufacturing operations, it may be possible to replace the hydrate of alumina by clay, deprived of its iron by a treatment with hydrochloric acid, and afterwards washed.

Independently of this formula, two more have been made known:—

According to Robiquet, a mixture of 2 parts of kaolin, 3 of sulphur, and 3 of dry carbonate of soda are heated in a clay retort until vapors cease to be disengaged. After cooling, the retort is broken, the powdered mass is washed with water, and the remaining powder is heated again until the sulphur is expelled.

Tiremon melted 1075 parts of crystallized carbonate of soda in its water of crystallization, and added 5 parts of red sulphide of arsenic, a quantity of gelatinous alumina equal to 7 parts of calcined alumina, 100 parts of sifted clay, and 221 parts of sublimed sulphur. The mass was carefully evaporated to dryness in a crucible, and then calcined at a red heat. Lastly, the product was kept again at a dull red heat in a covered dish, and stirred constantly for two hours.

We shall now add further particulars on each of the modes of preparation, with the exception of the Guimet process, which is still kept secret.

A. *Guimet Process.*

The *Société d'Encouragement* proposed, in 1824, a premium for the manufacture of an ultramarine possessing all the qualities of that extracted from *lapis lazuli.* This premium was awarded to Mr. Guimet, on December 3d, 1828.

We here reproduce an extract from the report made by Mr. Mérimée, in the name of the committee on chemical arts.

"In 1824, you proposed a premium of 6000 francs for the manufacture of an ultramarine blue possessing all the qualities of that extracted from lapis lazuli; this problem, to which you attached great importance, is completely resolved.

"Mr. Guimet, a graduate of the polytechnic school, obtained, one year ago, results which you would have applauded, but he thought that his work was not complete as long as he could see new improvements.

"At that time several artists made the trial of his ultramarine, and certified that they found it equal to that imported from Italy. The experiment may be seen in the *Apotheosis of Homer*, painted by Mr. Ingres on the ceiling of the gallery of the museum. The drapery of one of the principal figures is painted with Mr. Guimet's ultramarine, and no other painting presents such a bright blue.

"Neither has your committee on chemical arts neglected the experiments by which the indentity of quality of the new color with that extracted from lazulite, may be ascertained. It has verified in it all the characteristics of a pure ultramarine.

"This discovery will mark an epoch in the history of painting; it is one of which the chemical arts may be proud, etc."

Chaptal, the President of the Society, while presenting the premium to Mr. Guimet, remarked that Mr. Horace Vernet, in a very large picture, *the Battle of Fontenoy*, had employed Guimet's ultramarine exclusively, which he considers as superior to that prepared from lazulite.

So much for the Guimet process.

B. *Gmelin Process.*

The process of Mr. Guimet being still kept a secret, Gmelin, professor of chemistry at Tubingen, has published the following process for the manufacture of ultramarine. Although it may be advantageously modified in several ways, we present it as given by the inventor.

"Silica and alumina, in the hydrate state, are prepared—the first, by smelting finely powdered quartz with four times its weight of carbonate of potassa, dissolving the fluid mass in water, and precipitating by hydrochloric acid; the second, by precipitating a solution of alum with ammonia. These two precipitates should be carefully washed with boiling water. Then the proportion of the dry substance is determined by calcining a small quantity of the wet article. A certain quantity of hydrated silica, the weight of which is noted down, is dissolved in a solution of caustic soda, which should be as saturated as practicable. For every twenty-two parts of silica (calculated as anhydrous), there are added seventy parts of alumina (also calculated as anhydrous), and the whole is evaporated down to the state of a wet powder, taking care to stir the mixture during the whole operation.

"Two parts of sulphur and one of dry carbonate of soda are gradually brought to a middling red heat in a Hessian crucible, with a well fitting cover. When the mass is fused, the above mixture is projected into it by very small quantities at a time, and before new additions are made, the effervescence due to the escape of steam must have ceased. The crucible is left one hour longer at a moderate red heat, and then allowed to cool off. It contains ultramarine, mixed with an excess of sulphide of sodium, which is separated by washings. If the color contains an excess of sulphur, the latter is expelled by a calcination at a moderate heat. If all the portions of the ultramarine are not thoroughly calcined, the finest parts are separated by levigating the finely powdered substance in water.

"Ultramarine resists fire and alkalies, but not the action of certain acids."

C. *Tiremon Process.*

Take—

Sifted powder of the crude clay of Dreux . .	100	parts.
Gelatinous alumina, corresponding to an anhydrous proportion of	7	"
Dry carbonate of soda (400 parts), or crystallized .	1075	"
Sublimed sulphur	221	"
Sulphide of arsenic	5	"

Mix with the carbonate of soda, melted in its water of crystallization, the powdered sulphide of arsenic, and when the latter has become partly decomposed, add the washed gelatinous alumina, which is obtained by the precipitation of alum with carbonate of soda. Lastly, add the clay and the sublimed sulphur, which have been mixed beforehand. When the mass has become compact by evaporation, it is introduced into a covered crucible, which is heated slowly at the beginning in order to expel all remaining dampness, and then brought to a red heat. The fire should be conducted in such a manner that the product is agglutinated (sintered), but not fused.

After cooling, the product is heated again to expel the excess of sulphur, and then ground and washed in pure water. The powder which remains in suspension in the liquid, is collected upon a filter. When the mixture has been well made the whole may be employed, otherwise many portions remain colorless. There are brown fragments, resulting from the corrosion of the crucible, when the mixture has been completely fused. These defects do not appear if the operation has been conducted with the proper care. The blue is drained upon the filter without further washings, and dried. The product is of a fine bluish-green; and, if it be heated for some time, with occasional stirrings, it acquires a very handsome blue color.

D. *Weger Process.*

Preparation.—Grind together 8 parts of pure ferruginous clay (bole), $\frac{1}{2}$ part of hydrated alumina, 9 parts sublimed sulphur, and 8 parts of fused caustic soda, dissolved in 20 parts of water. When a homogeneous paste has been obtained, it is heated for one or two hours in a glass or porcelain retort, until there are no longer steam or sulphur fumes distilled over. The porous and greenish residue is then calcined in a Hessian crucible, in order to remove the excess of sulphur, and then (when cold) washed with pure water. The bluish-green powder is again calcined in a flat dish, which is covered and brought to an incipient red heat. During this operation, which lasts about one and a half hours, the powder is constantly stirred. Lastly, the color is washed and levigated (floated).

When the porous green mass, called ultramarine green, and obtained from the first calcination, is broken into pieces of the size of a pea, and exposed to the air for some time, it becomes transformed into a magnificent ultramarine lazulite blue, under the influence of the dampness in the air.

When dry caustic soda is thoroughly mixed with the indicated proportions of clay, alumina, and sulphur, and the mixture packed tightly in a Hessian crucible, there is obtained, after one to two hours of calcination at a clear red heat, a product which, when cold, possesses a pink-red hue, very handsome and uniform.

Green ultramarine, in the opinion of Mr. Weger, is a combination of blue ultramarine with a double proportion of sulphur. Therefore, by expelling the excess of sulphur by calcination, the second color is obtained from the first.

Ultramarine for printing.—The preparation of a printing color with ultramarine is very simple. A good quality of ultramarine is very finely ground, and mixed with linseed, or nut, or purified poppy oil. If the latter cannot be had, some old and perfectly clear oil may be used. One-twentieth of hydrated alumina, like that employed in the preparation of the ultramarine, is also added. Then a small quantity of good white Venice soap is finely ground upon the slab. In order to ascertain whether a sufficiency of soap has been added, a brush charged with the color is dipped into pure water, and we observe whether the color and the water mix well together or not. If the mixing be satisfactory, the proportion of soap is sufficient, because an excess will change the hue of the color. However, in case the printing mixture should be too compact, a little soap water, of which a supply should be kept at hand, may be added.

It is possible to print with this mixture upon tissues of cotton and wool, and even upon silk and paper. The color does not become hard, as is the case when the thickening is gum.

Miniature painting itself will find in this color vigorous and pure tones, and every intelligent artist sees the advantages it presents.

For theatrical decorations and paper hangings, where glue size is employed, the above mixture can be applied with the greatest success. It will impart an unequalled brightness and purity of color to flowers, fruits, shadows, etc., without any danger of the paint scaling off.

E. *Pruckner Process.*

Mr. C. P. Pruckner, manufacturer at Hof, in Bavaria, has published a memoir on the manufacture of ultramarine blue, which has been translated and printed in the *Technologiste*, v. 6, pages 299–345. We borrow from it the following description, and we note that the raw materials are clay, sulphate of soda, charcoal, and an iron salt, which is generally green vitriol.

"The clay employed in the manufacture of artificial ultramarine has the greatest influence upon the color produced; and it is likely that the failure of many experiments is due to the use of a clay holding too much iron. I use a white clay, remaining white after calcination, and which, therefore, contains very little iron. It is a kind of kaolin, of a dull color, which sticks to the tongue, forms with water a paste possessing little plasticity, and which is found in the principality of Reuss, near Roschitz. It is employed in the manufacture of porcelain, and contains from forty-two to forty-three per cent. of alumina. It is evident that, the other conditions being the same, the more aluminous clay is to be preferred.

"In the manufactory of Nuremberg, the clay most generally employed is a white sigillaria earth (*bolus alba*), which comes from Teschenrenth, in the High Palatinate.

"At Nuremberg, the sulphate of soda resulting from the preparation of hydrochloric acid is bought, either already refined, or in the crude state. In the latter case, it is refined in the color works, and this operation, which we shall examine further on, is intended to remove the free hydrochloric acid and the iron salts, which impair, and even destroy, the blue color of the ultramarine.

"Roll sulphur is too well known to need explanation.

"The charcoal from dry wood answers all that is required of it. Mineral coal is sometimes employed, and it should give the least amount of ferruginous ashes.

"The calcination of the mixtures is effected in muffles, heated in a reverberatory furnace, since it is much more easy to regulate the temperature and to watch the operation, than when crucibles are employed. These muffle furnaces, in the clear, are from 0.9 to 1 metre in width and length. The muffles themselves are from 0.55 to 0.60 metre wide, and from 0.30 to 0.37 metre high. In order to save fuel, 2 or 3 may be placed in the same furnace. The muffles are constructed of fire clay, in the same manner as the pots of glass works. Their front openings may be closed by cast-iron doors sliding upon rollers. These doors and the back parts of the muffles have each a narrow slit, for watching the operation and giving passage to the air. It is well understood that the furnaces are provided with dampers for regulating the draft and the temperature. The durability of the muffles is increased by supporting them upon three arches or brick walls resting upon the bed of the furnace. The spaces between these walls form flues from 0.20 to 0.23 metre square. When the fuel is charcoal, it may be introduced by an opening on top, as in assay furnaces.

"The conversion of the sulphate of soda into sulphide of sodium is effected in a furnace analogous to those employed in the manufacture of soda. In our works I have replaced the single lateral fireplace by two smaller ones, opposite to each other, and I have found by experience that this disposition gives a saving of time and labor, especially when the bed of the furnace is more than 2 metres in length.

"Let us now pass to the preparation of the raw materials, and to the manufacture of ultramarine blue.

"The dry clay, coarsely broken with wooden stampers, is placed in rectangular wooden vats, 2 metres long and 1 metre wide, where it is covered with water, and left to rest for several days. The resulting paste is then floated, as in porcelain works, for separating the sand and the coarse portions. The purified clay, in the state of soft paste, is kept under a shed, and its yield in dry clay is accurately determined each time that it is used for the preparation of ultramarine.

"The purification of the crude sulphate of soda is done by calcination in a reverberatory furnace, by which the free hydrochloric acid is expelled. The crude salt is broken into pieces of about 1 cubic decimetre, and plunged into water for a very short time, because experience has proven that the free acid is much more easily removed from the wet than from the dry salt. The furnace is filled with these lumps, with sufficient spaces left for the free access of the flame. The temperature is gradually raised to an incipient red heat, and is maintained until there is no free acid left. The calcined salt is immediately broken, under stamps or between stones, into grains of the size of blasting powder, which are mixed with the charcoal and slaked lime, in revolving tuns. The proportions are:—

Sulphate of soda	100 parts.
Powdered charcoal	33 "
Lime slaked in the air	10 "

"The ground mixture is spread upon the bed of the reverberatory furnace, and covered 3 to 4 centimetres deep with slaked lime, which is compressed with a flat iron shovel. All the doors of the furnace are then closed, and when the mass is thoroughly in fusion, it is rapidly stirred, and a few shovelfuls of charcoal dust are thrown in. The bath is left undisturbed for some time, until gas jets no longer burn at the surface. The sulphide of sodium is then removed with iron ladles, and poured into shallow cast-iron moulds, in which it solidifies.

"The sulphide of sodium and the carbonate of soda thus obtained are dissolved in boiling water, and the liquor is left to settle, out of contact of the air, in tubs, in which it deposits carbonate of soda, sulphate of soda, and charcoal in very minute particles. The sulphate of soda is treated in the aforesaid manner for another operation, and it is very important that all of the charcoal should be deposited, because a trace of it is sufficient to impair the brightness of the ultramarine. The clear and decanted solution is then heated, saturated with powdered sulphur, and concentrated by ebullition until it contains 25 per cent. of dry bisulphide of sodium, and marks about 25° Bé. From 40 to 50 parts of sulphur are employed for each 100 parts of fused sulphide of sodium.

"After the solution of sulphide of sodium has deposited the slight excess of sulphur contained in it, it is decanted into glass carboys, which are carefully closed, in order to prevent the contact of the air.

"The raw materials being prepared, the preparation of ultramarine is as follows: 50 kilogrammes of the above solution of sulphide of sodium are evaporated in a shallow cast-iron pan to a syrupy consistency; then a quantity of washed and wet clay, corresponding to 12.5 kilogrammes of dry clay, are added to it, and the whole is thoroughly mixed with an iron spatula. While the mass is still pasty enough to be stirred, there is added to it a solution of 150 grammes of sulphate of iron, free from copper, which is also carefully mixed. The stirring is continued until the mixture is entirely dry, when the substances are finely powdered.

"This powder is charged into the muffles, and spread in layers 6 to 8 centimetres deep, which correspond to a weight of 15 to 20 kilogrammes. The fire is continued for about one hour after the material has become red, and frequent stirrings are given, at the same time that the air is allowed free access. The mass becomes successively colored a liver color, then red, green, and blue. This operation requires a great deal of attention and practice, because too little heat produces no ultramarine, and an excess of temperature impairs the beauty of the color.

"The substance is then removed from the muffle, and purified by washings with water. The liquors, which contain sulphate of soda and sulphide of sodium, are generally thrown away, but they might be used for the preparation of the sulphide of sodium. The precipitated ultramarine is collected and drained in cloth bags, and then dried in a stove-room. Its color is generally a dark green or a blackish-blue.

"The dry mass is finely ground, passed through a silk sieve, and calcined again by portions of 5 to 7 kilogrammes, in muffles kept specially for this operation, and which are 45 to 50 centimetres wide, and 80 to 90 centimetres long. A dark red heat is sufficient for this calcination. As soon as the blue color begins to appear, the powder is constantly stirred with an iron tool, until the whole is of a pure blue. The operation lasts from one-half to three-quarters of an hour, and there is no advantage in continuing it longer, or in having a more intense fire. The powder is removed, and left to cool in the air upon granite slabs. It often happens, but not always, that the color acquires, while cooling, greater brightness and beauty.

"The ultramarine blue is afterwards ground under granite stones, 1.5 metres in diameter, then washed and floated and sorted, according to its degree of fineness, into the numbers $\frac{0}{0}$, 1, 2, 3, 4, etc.

"An excellent method for ascertaining the quality of ultramarine blue consists in heating it in a glass tube, placed upon a lighted alcohol lamp, and through which is passed a stream of hydrogen. The pigment will be the better and the more durable, as its blue color is longer in disappearing. Native ultramarine loses its color only after one or two hours, or even longer; the best artificial ultramarine of Nuremberg (mark 0) ceases to be blue after half an hour, and the inferior quality (mark 5) after a few minutes only."

F. *Winterfield Process.*

Mr. Winterfield has proposed a process for the manufacture of ultramarine blue, which he claims to give a produce as fine as Guimet's ultramarine, and at a very low price.

"200 parts of soda ash (from the evaporation of the mother-liquors of the crystallized carbonate of soda) are dissolved in boiling water, and there are added 100 parts of powdered sulphur, 4 of sulphate of iron dissolved in water, and 100 parts of powdered clay. The whole is thoroughly mixed and evaporated to dryness. The dry and finely powdered mixture is introduced into vessels of fire-clay, holding about 4 to 5 kilogrammes, and which may be closed with a clay cover. These vessels are heated in a furnace, and their contents are stirred now and then with an iron rod. When the mass begins to sink down, and acquires a blue-black coloration, passing to a green when cold, this operation is finished. For quantities of 5 kilogrammes, about four hours of continuous calcination are necessary. The cooling of the mass should take place out of contact with the air, the cover is therefore carefully luted upon the vessel. The cold substance is then coarsely broken, dirty-looking fragments are removed, and the remainder is washed with hot water. The still wet powder is finely ground. By this treatment, and under the action of the air, the green color passes to a fine blue. The clay employed is not very plastic, and is quite free from iron. Its color, before calcination, is a grayish-white. It is strongly calcined, in order to destroy the organic substances which may have been present, and then finely ground before use. The soda ash requires also to be calcined, in order to destroy the organic substances. The best vessels for this operation are a kind of fire-clay retorts, placed obliquely in the furnace, so that their opening is not exposed to the fire. The aperture is closed with a perforated cover, through which the stirring rod passes."

G. *Brunner Process.*

Mr. C. Brunner has published in the *Technologiste*, vol. 8, pp. 110–162, a very interesting memoir on the manufacture of artificial ultramarine, from which we take the following extracts:—

Before explaining the process itself, says he, which I have verified by a great many experiments, I shall make some remarks on the choice of the raw materials, and he continues:—

1. *Silica.*—I have used a gravel, or coarse silicious sand, found near Lengnau, Canton of Berne. It is known in the country under the name of *Hupererde*, and is employed as a cement in the manufacture of fire-bricks, crucibles, and other articles, which must stand a very high temperature.* I have always used it perfectly ground and floated.

2. *Alumina.*—Instead of this substance, I have employed the potassa alum; and, although a small proportion of iron does not appear disadvantageous, I advise purifying the alum by a second crystallization. I have heated it until it acquires the properties and the appearance of the *alumen ustum* of the pharmacopœia. On a small scale, this operation may be performed in a silver dish; but in manufacturing works a special furnace will be needed. At all events, it is tedious work. The burnt alum is then pulverized, and a sample of it is calcined at a moderate red heat in a platinum dish, in order to determine the proportion of water it still contains. This determi-

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* The analysis of this sand is as follows:—

Silica	94.25
Alumina	3.03
Lime	1.61
Oxide of iron	0.94
Loss	0.17
	100.00

nation is not very accurate, because, according to the degree of red heat used, there are variable proportions of sulphuric acid disengaged with the steam, but it is sufficiently accurate for practice.* The burnt alum is kept in well-closed vessels.

3. *Sulphur.*—For the calcination of the mixtures, ordinary sublimed sulphur may be used; but in the last combination with sulphur it is better to purify it by distillation.

4. *Charcoal.*—The ordinary wood charcoal is finely powdered.

5. *Carbonate of soda.*—The crystallized carbonate of soda is made to effloresce in the air of a hot room, and the resulting powder is heated in a dish until all the water disappears.

The preparation of the ultramarine is made in the following manner: A mixture is made of—

Silica (huper)	70	parts.
Burnt alum (calculated anhydrous)	240	"
Powdered charcoal	48	"
Sublimed sulphur	144	"
Anhydrous carbonate of soda	240	"

In order to obtain a thorough mixture, the materials are first incorporated together in the ordinary manner, in a mortar or dish, and then in a powdering apparatus, made of a thick copper flask, tinned inside, and holding about 2 litres. I put in from 15 to 30 grammes of the mixture, and from 600 to 700 grammes of coarse granules of cast-iron. The flask is closed, and shaken vigorously for eight or ten minutes, and

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* Further experiments have demonstrated that powdered alum, dried in the air, may be successfully employed; the tedious operation of burning it may therefore be dispensed with.

the contents are sifted upon a metallic sieve, which retains the iron granules.

The success of the operation depends especially on a careful and thorough mixture. The powder must be really impalpable, and an ordinary magnifying glass should show no difference of coloration in the particles.

A Hessian crucible is then entirely filled with this mixture, and closed with a luted cover. The crucible is rapidly raised to a moderate red heat, which is maintained for one hour and a half. The degree of temperature is important, but, after a little practice, it is easily learned; at all events, an excess of heat is to be avoided. When the operation is successful the cold contents of the crucible appear as a sunken and porous mass, partly greenish-yellow and partly reddish-yellow, resembling liver of sulphur, and occupying about two-fifths of its former volume. If it be hard and fused, brown, and of a still more reduced volume, the heat has been too great.

The porous pieces are easily detached from the crucible, and are thrown into water. The mass softens, and there results a solution of sulphide of sodium, and a greenish-blue powder which precipitates. The powder is washed several times with water, which may be hot, and until the liquor becomes tasteless. The residue is then dried.

The washed product is in the state of a light powder, of a clear ash-gray color. A small sample is heated in a porcelain dish with a small quantity of sulphur, in order to see whether the combustion of the latter substance causes it to assume a bluish tinge. This coloration will always be feeble, about like that of blued linens.

This product is then intimately mixed with an equal weight of sulphur, and one-and-a-half times its weight of anhydrous carbonate of soda, in the manner already explained. Another calcination is made at the same temperature, and the volume of the mass diminishes again, but less than formerly. After cooling, the contents of the crucible are washed in water, and the residue is dried.

This new product, calcined with sulphur in a porcelain dish, should, this time, acquire a more intense bluish hue.

The amount of washed substance is about the same as after the first calcination. A third calcination with sulphur and carbonate of soda, in the proportions previously stated, is followed by a more thorough washing. It is even useful to boil the product in water, and to finish the washing upon a filter, until the liquors are no longer colored black by the acetate of lead. The future color of the product depends partly upon the fulfilment of these precautions.

Another test with burning sulphur is made to see whether a fine blue color will appear. If it be satisfactory, the product passes to the finishing operation; in the contrary case, it is again calcined with sulphur and carbonate of soda. Ordinarily, three calcinations are sufficient; but, if they have been effected at too low a temperature, a fourth calcination is necessary.

The dry and bluish-green powder is passed through a gauze sieve, in order to separate a few hard brown granules, which come from the crucible or from the compound itself fused at certain points.

The last operation, that is, a combustion with sulphur, is made upon a plate of cast-iron, on the surface of which there is spread a layer, two to three millimetres thick, of pure powdered sulphur. An equal quantity, or a little more, of the dry powdered product is dusted over the sulphur by means of a sieve. The cast-iron plate is heated upon a charcoal fire until the sulphur becomes inflamed, and the temperature should be such that all the sulphur will burn out without the product being too much calcined. It is sometimes necessary to remove the charcoal fire. On a large scale, this combustion should be effected in furnaces provided with doors for regulating the access of the air, and, therefore, the intensity of the combustion. This operation is repeated three and even four times with the same powder, which, after each combustion, is removed from the plate and ground. When the product has attained its greatest intensity of coloration, the whole operation is finished. In the manufacture of large quantities, it will be well to base the mode of working upon experiments made on small samples, which are mixed with half of their weight of sulphur, and spread upon a cast-iron plate.

This last operation somewhat diminishes the volume of the product, and imparts to it a porous and flaky appearance. I have been unable, with a magnifier, to discover any sign of crystallization. For its employment, the product requires to be ground again finely. The yield in finished product is about one hundred and sixty parts of the materials previously indicated.

Before finishing, I shall point out several experiments, which, in my opinion, throw some light upon the origin, the formation, and the chemical composition of artificial ultramarine.

During the first calcination of the mixture, there is already formed a chemical compound of sulphur, sodium, silica, and alumina. This compound is now but slightly colored, and sometimes not at all. That there is a combination is proven by the fact that the well-washed powder is decomposed by acids; sulphuretted hydrogen is disengaged, and gelatinous silica is precipitated. The addition of powdered charcoal to the mass, during this first calcination, is not absolutely necessary, but it prevents the fusion of the mass. Such addition is useless for the other calcinations.

During the second calcination with sulphur and carbonate of soda, the proportion of sulphur, and possibly of sodium, increases, although the weight of the product is not much greater. The increase in the proportion is certainly not considerable, and is counterbalanced in part by the losses of manipulation.

In this state, the washed and dried product, although but slightly colored, possesses a real bluish-green hue, which, after combustion with sulphur in the open air, passes to a pure but pale blue.

In the next operation, that is, a third calcination with sulphur and carbonate of soda, the proportion of sulphur still increases. The washed and dried product is of an intense blue color with a green reflex, and is finished, although it is yet wanting in the remarkable brilliancy possessed by ultramarine.

Some persons may think that these three operations may be united in one, whether by calcining longer, or by increasing the proportion of the materials; but direct experiments made in that direction have not furnished satisfactory results.

The subsequent combustion with sulphur is, theoretically speaking, the most remarkable part of the whole operation. The product acquires by this treatment its real coloration, and it increases in weight from 10 to 20 per cent. This increase is variable, and depends partly on the quality of the product before the combustion, and partly on the manner in which this combustion is conducted.

It may seem difficult to arrive constantly, by three calcinations, at precisely the same degree of color and quality; but in practice, when large amounts of materials are worked at a time, a greater regularity is obtained. I insist upon the point, that a great degree of comminution and a perfect mixture of the materials, produce a great yield. Indeed, if we neglect these precautions, the product will be filled with a quantity of whitish specks, and will never acquire a fine color; it may even acquire a brownish hue. During the combustion with sulphur, the powder increases in weight. This increase is not always constant, and may, by combustions repeated ten and even fifteen times, amount to 20 per cent. After three or four successive combustions, the color has acquired its greatest intensity, and the increase of weight may be 5 to 10 per cent.*

In order to compare the increase of weight with the proportion of sulphur, I have determined this in samples of the mixture before the calcination, and after each heat.

The following analysis gives the centesimal composition of the ultramarine which has not been burned with sulphur:—

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* Clement and Desormes had already published the fact, that real ultramarine increases in weight about 1 per cent., when it is heated in oxygen.

Silica	35.841
Alumina	27.821
Lime	2.619
Oxide of iron	2.475
Sodium	18.629
Sulphur	5.193
Oxygen (calculated from loss)	7.422

And as 100 parts, after the combustion with sulphur, become 110.16, holding 12.811 of sulphur, while the other substances are not changed, it results that ultramarine burned with sulphur should be composed of—

Silica	32.544
Alumina	25.225
Lime	2.377
Oxide of iron	2.246
Sodium	16.910
Sulphur	11.639
Oxygen (calculated from loss)	9.039

If now we distribute the oxygen between the sulphur and the sodium, on the supposition that they form sulphate of soda, we have, instead of the last three elements :—

Sulphate of soda	20.157	= 17.421 sulphide of sodium.
Sodium	10.337	
Sulphur	8.084	

We see, therefore, that the sulphide of sodium is in the monosulphide state, since theory requires 10.337 of sodium and 7.149 of sulphur.

It is evident that this mode of representation, like those used for complicated compounds, cannot be absolute, and presents only a theoretical interest. Sulphur may be combined with the sodium, calcium, and iron; in which case a part of the sodium should be calculated as soda. But these speculations cannot be verified by analysis.

If, after ultramarine has reached the greatest coloring intensity by its combustion with sulphur, this treatment be continued, there comes a time when the product no longer increases in weight. If it be heated without sulphur, its weight diminishes, and its blue color becomes lighter, resembling that of certain kinds of native ultramarine, and it often acquires a slightly lilac hue. Besides these chemical changes, there is also another mechanical transformation; the powder ceases to be light and flaky, and becomes dense and granular. Mr. Brunner, however, has not always succeeded in producing this change. In many samples found in the market this phenomenon is easily produced; in others, it is less apparent, even after heating for hours together. An ultramarine modified in this manner and treated by hydrochloric acid, does not disengage hydrosulphuric acid, and contains, therefore, no unoxidized metallic sulphide. It may be thought that there should be an increase of weight resulting from oxidization; but the diminution in weight may possibly be explained by supposing that, while part of the sulphur of the sulphide of sodium burns, the resulting soda combines with the silica or other elements of the compound. Since the volatilized sulphur possesses a greater weight than the oxygen which takes its place, there must result a lesser yield.

These pale ultramarines, at all events, may be usefully applied in the arts, and it is likely that some may be found among the manufactured products.

There are still three points to be decided:—

"1. How far necessary is the proportion of lime found in nearly all commercial ultramarine blues?

"2. Is the presence of iron useful, or unfavorable, to the production of the color?

"3. Is soda absolutely necessary, or is it not possible to replace it by potassa?

"The presence of lime is not absolutely necessary, and this is proven by the small proportion of it in the indicated mixtures. Moreover, I have checked the exactness of this conclusion by direct experiments, in which I have added as much as 8 per cent. of lime in certain mixtures. There was no difference whatever between the products obtained and those made without lime.

"Iron is neither important nor absolutely necessary. Indeed, a mixture made according to the preceding formula, but with materials free from iron,* and without using iron granules during the pulverization, has given a product entirely similar to that prepared in the ordinary manner. However, the fine artificial ultramarine of Guimet, and the native one imported from Rome, show the presence of iron by delicate analytical tests.

"It does not seem important to me to investigate whether a large proportion of iron is to be avoided in the color; but, *a priori*, it seems that it should be so.

"Lastly, a question which appears to me very interesting is, whether the blue coloration is principally due to a sodium compound, or if it cannot be produced with potassa.

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* The silica was prepared by calcining the *huper* with the carbonates of soda and potassa, filtering, and precipitating the silica with hydrochloric acid. The iron in the charcoal has not been considered.

"I have, therefore, conducted an operation according to the preceding formula, with the exception that the carbonate of soda was replaced by carbonate of potassa, prepared from the combustion of cream of tartar. After three calcinations of the mixture there was obtained a white mass, which, being burned with sulphur, did not acquire any blue coloration, although it disengaged an abundance of sulphuretted hydrogen by a treatment with hydrochloric acid.

"It is then demonstrated, in conformity with the assertion of Gmelin, that potassa (without soda) does not produce a blue ultramarine, but that a similar colorless compound is obtained. This experiment seems to be a further proof that the blue color is not due to the presence of iron."*

H. *Dippel Process.*

In a pamphlet published by Mr. J. P. Dippel, of Cassel, on the preparation of artificial ultramarine, this chemist recommends the following process as having been for a long time advantageously practised in manufactories.

The materials are clay, Glauber salt (sulphate of soda) with an excess of sulphuric acid, bituminous coal, and sulphur; each of which should possess certain qualities. The first three are mixed in certain

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* I had already written the above memoir when one of Mr. C. P. Pruckner, upon the manufacture of ultramarine, fell into my hands. Time and circumstances prevented me from experimenting with his mode of preparation, which resembles that of Gmelin, and to compare it with mine. It seems, however, possible to arrive at the same results in different ways, although I differ from the opinion of Mr. Pruckner, who believes that the presence of iron is absolutely necessary.

proportions, and then brought to a red heat in a crucible. After cooling, the mass is removed from the crucible and then calcined again in a tube, with the access of the air. The product is afterwards steeped in water, ground wet, and lastly heated to produce the blue color in the following manner: the powder is mixed with sulphur, and heated in the presence of just enough air to cause an incomplete oxidization of the sulphur. When the fine blue color has been developed the pigment is ground again, then floated and dried.

J. *Habich Process.*

Mr. G. C. Habich has published in the *Technologiste*, vol. xvii. p. 411, the following remarks on ultramarine and its manufacture:—

"Two kinds of ultramarine blue may be distinguished from their behavior in presence of concentrated acids. When cold hydrochloric acid is poured upon ultramarine, the color disappears, part of the sulphur is disengaged as hydrosulphuric acid, and the other part settles with the remainder of the powder. It is then that there appears a characteristic difference due to the modes of preparation. When ultramarine has been manufactured from artificial aluminous silicates, gelatinous silica is precipitated. On the contrary, when white clay has been used, there is no production of gelatinous silica.

"When the manufacture of ultramarine took a foothold in Germany, the first named process was employed; and although it is too expensive, it nevertheless presents a real scientific interest.

"Soda, white sand, sulphur, and powdered bituminous coal were melted together, and the resulting mass being dissolved in water, gave a solution of polysulphide of sodium and of silicate of soda, with which another hot solution of alum was precipitated. The result of the decomposition was an abundant production of sulphuretted hydrogen, and a precipitate of silicate of alumina and of sulphur. This precipitate was washed, dried, and introduced into a boiling bath of soda and sulphur. The molten mass, when the operation was successful, crumbled in hot water, and deposited a very finely comminuted powder of a bluish-green color, called green ultramarine, which, being entirely deprived of soluble salts by a careful washing, was dried. This green ultramarine was then rendered blue by a calcination with sublimed sulphur, as we shall see further on.

"We see that this process, on account of the materials employed, was very expensive. On the other hand, we must acknowledge that the purity of color of the product was far superior to that of the ultramarines prepared with clay by the present process.

"This last process is more economical, and its mode of operation varies with different manufactures. I shall explain that which I found to succeed the best.

"Preference is given to that kind of white clay which is found in various localities, near Worms for instance, and which is called lenzine (lenzinite). It is thoroughly deprived, by floating, of all the sandy parts which may be mixed with it, then dried and finely powdered. 10 parts (in weight) of this powder are mixed with 22 parts of Glauber salt (anhydrous and free from iron), 3 of sublimed sulphur, and 3.5 parts of colophony.

"This mixture is charged into pots, made of a scarcely plastic clay, to which a certain proportion of sand is sometimes added. These vessels are made upon a potter's wheel, and, after a protracted desiccation, they are burned. Their shape is conical, thirty centimetres in diameter at the bottom, and of an equal height. The aperture of each, after the charge is put in, is closed with a cover, which is luted on with clay. The mixture should be strongly compressed.

"The pots are then placed in the same oven in which are burned the empty ones; but as the latter do not require as uniform a temperature as the former, they are put near the fireplace and near the chimney flue, while the central part of the oven is reserved for the filled pots.

"A heat in these furnaces lasts three days, and the fire should be maintained until the mass in the pots has sunk and has become agglutinated. After cooling in the furnace, the pots are broken, and the surface of the calcined mass is cleaned of any extraneous matter, which generally comes from the pots themselves. It is then coarsely ground, and calcined in a reverberatory furnace or in a cast-iron dish, as long as sulphur vapors are disengaged.

"This calcined mass is lixiviated with water, until most of the soluble salts are removed. The liquors are evaporated to dryness, and give Glauber salt.

"The washed bluish-green powder is ground again to a fine magma, under hard quartz stones, because soft stones become impregnated with the material, and crumble easily.

"The schlamm or colored magma is floated (levigated) in a special apparatus, which gives on one side a highly comminuted powder, and on the other a coarse article which is ground again.

"This levigated powder is thoroughly washed with water, until a sample ceases to be improved by the operation, or until two samples from two consecutive washings have exactly the same coloration. The pigment is then collected upon a filter, drained and dried. It has a pure, but pale bluish-green hue.

"The operation by which the blue color is made to appear is conducted in a horizontal cast-iron cylinder, placed above a fireplace and covered with brickwork. On the top of the cylinder there are several openings for charging the sulphur and allowing the access of the air. These apertures may be closed when desired. This cylinder also contains a stirring apparatus, the blades of which come very near to the bottom.

"This apparatus is about one-half filled with the powder, which has been passed through a fine hair sieve. The fire is then urged until all the material becomes red hot. For every 100 parts of sifted powder introduced into the cylinder, 6 parts of sublimed sulphur are thrown in through the apertures. As soon as the sulphur has caught fire the fire is removed, and the stirring apparatus is set in motion. A little while after, fresh fire is put upon the grate bars, and 3 per cent. more of sulphur is added. A moderate heat is continued, the mass is constantly stirred, and air is largely admitted, until the color has acquired its greatest intensity.

"When this color is left exposed for a long time to moist air, it may happen that it will agglomerate and form hard lumps. It is a proof that it still retains soluble salts, and that it has not been sufficiently washed."

K. *Gentele Processes.*

Mr. J. G. Gentele, a learned manufacturer, has published a very interesting memoir on the preparation of artificial ultramarine. We borrow from the *Technologiste*, vol. xviii. pp. 389–411, several extracts from this memoir.

"The preparation of artificial ultramarine blue is described in all the works on chemistry, but in a summary way, and without sufficient details for manufacturers. This manufacture, which was already important in respect to painting, has still gained in interest, since ultramarine has been successfully used for calico printing. This has determined us to lay before the public all the practical data which we have been enabled to collect in our own practice, or from the French and German works which we have visited.

"The manufacture of artificial ultramarine is divided into two distinct operations—first, the preparation of the green ultramarine; second, the transformation of the latter into ultramarine blue. The beauty of the final product depends on the quality of the former, and, therefore, the first operation requires all the attention of the manufacturer. I shall describe separately the preparation of each of these products.

1. *Manufacture of Ultramarine Green.*

"*Raw materials.*—The following substances are used, at the present time, for the preparation of ultramarine green:—

1. Aluminous silicate, kaolin for instance.
2. Anhydrous sulphate of soda, } sometimes in solution.
3. Anhydrous carbonate of soda, }
4. Sulphide of sodium, as a secondary product of the manufacture.
5. Sulphur.
6. Wood charcoal, or bituminous coal.

"All of these materials require to be carefully chosen, and to be submitted to certain preparatory operations. These operations generally require mechanical appliances, which form the heaviest outlay in the building of the works.

"The most advantageous *aluminous silicate* is porcelain clay, or kaolin, or a white clay, the composition of which should not be very different from that of kaolin. A small proportion of magnesia and lime is not objectionable; but a clay, holding more than 1 per cent. of oxide of iron, should be admitted only after previous experiments. Kaolins present all the desired qualities, and are not scarce, and French and German manufacturers have no difficulty in getting what they need. Formerly, ordinary clays were worked with an addition of alumina, artificially prepared; silica was also added to clays. At the present time all these costly additions are dispensed with by a judicious choice of clays, which, after calcination, should have a composition corresponding approximately to the formula $Al^2O^3,2SiO^3$. No account is taken of small proportions of lime, magnesia, and oxide of iron, and it matters not whether the silica is or is not entirely in chemical combination. It often occurs that clays in their natural state do not present the desired composition, from being mixed with sand and other mineral substances. But, as the mechanical operations to which the clays are submitted retain most of these foreign materials, it results that clays so treated are very near the indicated composition.

"The preparatory working of the clay, in order to remove its mechanical impurities, is effected in exactly the same manner as in porcelain works, that is, by levigation or floating. The washed clay is dried, slightly calcined, and then immediately ground to a fine powder. There are, however, manufacturers who do not calcine or grind it.

"The floating of the clay is done either by hand or by power. When the clay is slow to soften in water it is coarsely ground between two stones, and then made into a thin paste, which is allowed to deposit its coarsest impurities. The pure clay is stirred again in water, and the light particles settle in other tanks. After decanting the water, the pasty mass is collected and pressed in sacks, and dried by heat, or in the air upon porous slabs of plaster of Paris. When pure and washed kaolin is bought, it is evident that these manipulations are dispensed with.

"The slight calcination given to clay is effected in an ordinary reverberatory furnace, at a temperature not above the beginning of a cherry-red heat. By this operation the earth loses all its combined water, becomes friable, and ceases to be plastic; in fact, it can easily be powdered, which is the intent of this calcination.

"The clay is pulverized under stamps, or under a vertical stone revolving upon a horizontal one, and is then passed through a series of fine metallic sieves. The coarse portions are ground again.

"If the *sulphate of soda* be employed in the anhydrous state its quality should be considered. It should not contain free acid, and if it be sold by the soda manufacturers, free from iron and lead, so much the better. When such a salt cannot be had, a Glauber salt is bought which contains no free hydrochloric acid. It is dissolved in water, and the excess of sulphuric acid is saturated with a small quantity of milk of lime, which at the same time precipitates the oxide of iron. The clear liquor is decanted and made to crystallize. The sulphate of lime and the excess of lime remain in the deposit. The crystallized sulphate of soda is slowly dried in a cast-iron kettle, or, what is better, upon slabs of fire-clay on the bed of a reverberatory furnace. In either case the product is an anhydrous Glauber salt (sulphate of soda). The clear liquors may also be directly evaporated, without being made to crystallize, in a pan which is always kept full of fresh liquor. At a certain degree of concentration an anhydrous sulphate is precipitated, which is fished (removed) with perforated ladles. This salt is deprived of all adhering water by a slight calcination in the reverberatory furnace.

"The Glauber salt, either bought anhydrous or rendered so by the above process, is ground and passed through sieves, which should not be too fine. The ground salt should be kept in closed vessels, because it may become compact by attracting atmospheric moisture. This salt may be bought of manufacturers who evaporate pure liquors and calcine the residue afterwards; but it is difficult in ultramarine works to dispense with the necessary apparatus for this treatment, because, during the course of the operations, there are produced washing liquors containing sulphate of soda, which ought to be evaporated. The salt, thus prepared, always contains small proportions of chloride of sodium and of sulphate of lime, which form no impediment to the manufacture.

"The *carbonate of soda* is also used in the anhydrous state, and it can be bought as pure and as dry as desired. The dry carbonate of soda (soda ash) of the manufacturers is the salt precipitated during the evaporation of the liquors of crude soda, and calcined afterwards. A small quantity of sulphate of soda in it presents no inconvenience. This carbonate of soda is powdered like the sulphate, and is kept in the same manner.

"The ultramarine works which do not use directly the *sulphide of sodium* in solution, should be provided with a certain number of evaporating kettles, made of wrought or cast iron, and heated by the waste heat of the calcining and evaporating furnaces. The liquors are evaporated to dryness, and are constantly stirred towards the end of the operation. The sulphide of sodium is powdered, and kept, in the same manner as the sulphate and carbonate of soda. In making the mixtures this sulphide of sodium is reckoned as a simple sulphide.

"The *sulphur* employed is in refined rolls. It is also ground and passed through a fine sieve.

"The *carbon* necessary in the manufacture of ultramarine may be derived from bituminous coal, or from the charcoal of any kind of wood. The impurities of the large pieces of charcoal are removed by sifting, and those of the small fragments by a levigation. The impurities, which are heavier, fall to the bottom of the tank, and the floating charcoal is removed and dried. The more caking kinds of bituminous coal are preferred, provided their percentage of ashes is small.

"The two kinds of coal are always reduced to a very fine powder either by trituration with common balls in a revolving cylinder, as is done for cannon powder; or by grinding with water in sand-stone or granite mills, until the coal or charcoal forms an impalpable powder, easily separated from the water. The settled powder is collected, drained, and dried upon shelves. It is again ground and sifted before use. This last method is very convenient for either charcoal or bituminous coal.

"While compounding the mixture, it is necessary that the component parts should be in the correct proportions, and, also, that the mixture should be thoroughly homogeneous. The more this condition is fulfilled the better the results. When dry materials are used it is advantageous to weigh small quantities of them, and to mix them in a trough with a spatula. The mixture is then passed through sieves of medium fineness, stirred again, sifted anew, and so on, until the proper result is arrived at. The sifting of the mixture of materials should be done by small quantities at a time, and no new material put upon the sieve until it is entirely empty.

"Another method has been adopted in several factories. Thus, instead of using the sulphate and the carbonate of soda, or the sulphide of sodium, in the dry state, they measure solutions of these salts, marking a certain hydrometric degree, which corresponds to a given proportion of dry salt. The powdered kaolin is put into these solutions, and the whole is evaporated to dryness. The powdered charcoal is sometimes added to them. The dried mixture is then slightly calcined in a reverberatory furnace, powdered, and rendered homogeneous by consecutive stirrings and siftings. Lastly, the powdered sulphur is added and mixed in the same manner.

"The respective proportions of the raw materials vary considerably with different manufacturers, nevertheless care should be had—

"1. That the soda, either as sulphate or carbonate, be in sufficient quantity to saturate half of the silica in the kaolin;

"2. That the proportions of sulphur and soda be such as to produce a bisulphide or a polysulphide of sodium;

"3. Lastly, that in the mixture there remain enough sulphur and sodium to form a mono-sulphide of sodium, when all of the green ultramarine, resulting from the silica and alumina, is extracted from the mixture.

"The German manufacturers compose their mixtures in a manner different from that of the French. The latter employ only the carbonate of soda, while the former use only the sulphate of soda, or a mixture of sulphate and of carbonate. In either case, the results appear identical. In the case of sulphate of soda, more carbon and sulphur are employed. With the carbonate of soda, no carbon is required, and a great deal of sulphur is needed. It appears that the German mode of manufacture is more economical.

"I now give the formulæ employed in factories, and which may be used for such mixtures:—

	I.	II.	III.
Kaolin, calculated dry	100	100	100
Anhydrous sulphate of soda .	83 to 100	—	41
Anhydrous carbonate of soda .	—	100	41
Coal	17	12	17
Sulphur	—	60	13

"During the course of manufacture, there is obtained a lye of sulphide of sodium, and a portion of this salt may be usefully substituted for part of the sulphate or carbonate of soda. This sulphide is introduced, either evaporated and dry, or in solution, according as the various substances are mixed dry or wet. In these solutions of sulphide of sodium, the proportion of sodium alone, and not that of sulphur, is to be considered. It has been ascertained that 100 parts of anhydrous carbonate of soda may be replaced by about 80 parts of dry sulphide of sodium; and 100 parts of dry sulphate of soda, by about 60 parts of dry sulphide.

"The principal operation now to be done with the mixture is its calcination. It is necessary that the mixture should be brought to the proper degree of high temperature, without the contact of the air, and that the heat should be maintained long enough to penetrate the whole mass as uniformly as practicable.

"An irregular and defective calcination never gives advantageous results even with the best mixtures. In order to operate under the best conditions this process employs vessels resembling crucibles or the seggars of porcelain works, which are heated in ovens built of fire-clays, and in the shape of small porcelain ovens. There is a great waste of heat in these kinds of furnaces, and in a majority of ultramarine works it is partly utilized in evaporating the mother-liquors or the wet mixtures.

"The crucibles or calcining vessels are made of good fire-clay, which should not become soft or break at the temperature required for the operation. They may be formed upon a potter's wheel, like flower pots; and if their shape is that of seggars, the diameter is 15 or 16 centimetres, and the height from 8 to 10. The top edge should be level. Only a small number of flat covers are needed, because with the seggar-like vessels the bottom of one becomes the cover of that upon which it rests.

"When crucibles are employed, their shape is represented by Fig. 52; and the cover is depressed so as to receive the bottom of the next crucible.

Fig. 52.

"This last shape appears to be the most convenient, because, although the crucibles may be placed close to each other, there is enough free space between them to permit the heat to circulate. With seggar-shaped vessels it is necessary to isolate each column, and then there is danger that it will topple over.

"The calcining furnaces are generally built one against the other, with a single partition wall. The following cuts give an idea of the shape which has been found to be the best:—

Fig. 53.

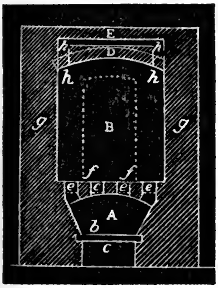


Fig: 54.

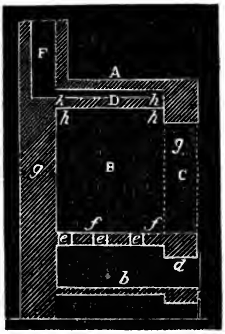
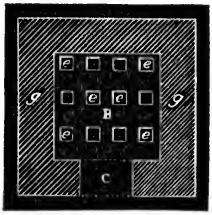


Fig. 55.



"Fig. 53 is a transverse section of the calcining furnace.

"Fig. 54 is a longitudinal section.

"Fig. 55 is a horizontal section near the bed of the furnace.

"A, fireplace; *b*, grate; *c*, ash pit with door; *d*, door of the fireplace; *e e e*, flues going from the fireplace into the calcining space or room.

"B, calcining room; *f f*, floor or bed of this room, perforated with the flues *e e e*, which may be rendered smaller by wedge bricks put into them; *g g*, brick walls. In front of this furnace there is a large charging door C, which is closed with fire-bricks during the calcination. The floor or bed of the furnace is made level with fire-bricks, placed on top of the arch which covers the fireplace. D is the arch closing the calcining room, and provided with four flues *h h*, for the escape of the heated gases, which are collected in the general flue E, and go, either under the evaporating kettles, or directly to the chimney.

"In other factories they use the round porcelain ovens with three fireplaces; but these furnaces take more room, and the fire is not so easily regulated as in the preceding one, with a single fireplace.

"In all ultramarine works there is a small experimental furnace, which contains from six to eight crucibles or seggar vessels. It is in it that the mixtures are tried before they are prepared on a large scale. This small furnace is especially useful for testing new qualities of clays, since the experiment is much more rapid than a chemical analysis. At the same time there is more certainty that the results obtained on a small scale will be reproduced on a large one.

"The composition or mixture to be calcined is put into the crucibles or seggars with a small shovel, and then strongly stamped in with a wooden tool, without, however, breaking the vessels. The calcining room is then filled nearly to the top with piles of these crucibles, and care is taken that the apertures of the flues are left free. The changing door is closed with firebricks without cement in the joints; but the outside interstices are filled with a plastering of sand and clay. The firing is then begun.

"We understand that it is indifferent whether the furnace be heated with bituminous coal, wood, or peat, provided the fireplace suits these different fuels.

"The temperature is slowly raised to a light red, or an incipient white heat. When beginning the manufacture, it is necessary to make a few trials of heat in the experimental furnace. The degree of heat is seen through an opening, 5 centimetres in diameter, left in the charging door, and which is closed with a movable clay plug.

"The time required for a heat, in the above furnaces, varies from seven to ten hours, with the indicated compositions. The less the excess of sulphide of sodium in the mixture, after calcination, the longer this composition requires to be heated, to arrive at a given result.

"When the calcination is complete, the furnace is left to cool, with all the apertures closed; and, as soon as the temperature has become low enough, the crucibles are removed and a new charge is put in. In this manner, three charges per furnace may be made in a week. The calcined mass in the crucibles has sunk and is grayish, and often yellowish-green. The crucibles are immersed into fresh water, or into the washing liquors of green ultramarine, and the contents are dissolved. The separated mass is then washed in appropriate tanks, with several waters, and the last liquors, which are weak, are reserved for solutions or washings, instead of pure water. The ultramarine thus obtained is composed of porous fragments, large and small, which are ground wet in mills similar to those employed for porcelain compositions. The operation is continued until a very great degree of comminution is obtained. The ground powder is then washed several times by decantation (that is, by stirring in water, settling, and removing the liquor), and then collected upon filters and dried. When the substance is dry, it is again stamped, and passed through fine hair sieves. In this state, it may be sold as green ultramarine, or transformed into blue ultramarine.

"Only a good quality of green ultramarine will permit of the preparation of a fine ultramarine blue. When, after the proper care in the operations, an inferior product is obtained, the cause of such a result must be found in the wrong preparation of the mixture, and, especially, in too small an excess of sulphide of sodium. The unequal coloring of a product should be attributed to a mixture which has not been made sufficiently homogeneous. When the crucibles break, the portions of material adjoining the cracks are colored blue by the action of the air; but this is no great inconvenience. Brown specks show that the heat has not been sufficient, and that all the carbon has not been burned. These defective portions should be washed and treated anew like clay.

"If, in the above indicated mixtures, we calculate the results of the reactions of their elements, without taking into account the accidental proportions of lime and iron, we find for the formula I.—

55.55 silica	in 100 parts of anhydrous kaolin.
42.00 alumina	
Lime, oxide of iron.	
43.72 soda	in 100 parts of andydrous sulphate of soda.
22.51 sulphur	
33.77 oxygen	
17.00 carbon.	

The result is composed as follows:—

(*a*) 67.83 silicate of alumina $\begin{cases}42.00 \text{ alumina,}\\ 25.83 \text{ silica,}\end{cases}$

(*b*) 59.63 silicate of soda $\begin{cases}29.91 \text{ silica,}\\ 29.72 \text{ soda,}\end{cases}$

since half of the silica has been taken from the alumina in the kaolin, and there remain—

(*c*) 19.00 sodium,
22.55 sulphur,

that is to say, there remains a mixture of a bisulphide, and of a monosulphide of sodium, in which the bisulphide contains 13.70 of sodium and 18.90 of sulphur, and the monosulphide, 5.85 of sodium and 3.65 of sulphur.

"If, from these elements A, we deduct those B of green ultramarine, as they result from my analyses* upon 143 parts of this substance, we shall easily understand how the blue color results. In the following subtractions, no account is taken of the small proportion of lime and oxide of iron held in kaolin, because these substances produce no reaction.

	Al^2O^3,SiO^3.	NaO,SiO^3.	NaS^2.	NaS.
A	67.83	59.63	32.60	9.00
B	67.65	57.09	15.07	
	0.18	2.54	17.53	9.00

"There remains therefore a notable excess of mono- and of bisulphide of sodium, which is afterwards washed out.

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* In a previous memoir, the author gives analyses of 10 commercial ultramarines, blue and green, and he infers from them that both green and blue ultramarines have an analogous composition, that is, an atom (old style) of silicate of alumina united with an atom of silicate of soda; without deciding, however, whether the green or blue color invariably belongs to these double silicates.

"In the mixture of formula II. the proportion of kaolin is the same as in formula I., and therefore its component parts are the same. The anhydrous soda gives—

58.64 soda, and there is, besides,
60.00 sulphur,
12.00 carbon.

"After the reaction, we have the same quantity of silicate of soda and of silicate of alumina as in the preceding case. The charcoal is sufficient for reducing all the soda; and there is also enough sulphur for reducing all the sulphuric acid, and forming with sodium 59.66 parts of bisulphide of sodium. If we operate the subtractions as above, we have—

	Al^2O^3,SiO^3.	NaO,SiO^3.	NaS^2.
A	67.83	59.63	59.66
B	67.65	57.09	15.07
	0.18	2.54	44.59

"There remains, in this case, a much greater excess of sulphide of sodium than in the preceding operation, and it is evident that the composition of the mixture may oscillate between more extended limits, since, besides the reactions in different proportions, there is formed only a certain excess of sulphide of sodium. However, it is also necessary that the carbon added should be burned.

"The calculation of the mixture of the formula III. furnishes analogous results.

2. *Manufacture of Ultramarine Blue.*

"Blue ultramarine is always prepared from green ultramarine, and this operation presents no difficulty. The transformation of the green product may be effected in different ways; but up to the present time, manufacturers use one method only, that is, a calcination with sulphur at a low temperature. The sulphur is transformed into sulphurous acid, and a portion of the sodium is oxidized, and is separated from the green ultramarine in the state of sulphate of soda. The sulphur held by this green ultramarine remains whole, but combined with only a small quantity of sodium.

"This calcination is done by two different methods, which may be called respectively the French and German methods, from the countries in which they are employed, although there are several German factories which use the French method.

"In the German mode of calcination, there are used small cast-iron cylinders, imbedded in brickwork, above a fireplace. The back part of each of these cylinders is not movable, and is provided with a hole for resting in it one extremity of the shaft of a revolving stirrer. The front part, made of wrought iron, is movable, and has several holes; one for the other end of the stirring shaft, a small one below, and a larger one above, for the introduction of the sulphur. All these openings may be closed at will. There is another hole on top of the cylinder for the escape of the vapors of burning sulphur, and an iron pipe is fitted to it, in order to prevent the escape of material during the rotation of the stirrer.

"This cylinder is charged, either by means of a small shovel passing through the upper opening, or by removing the front part, and immediately replacing it when the sulphur is in. At the same time, the shaft of the stirring apparatus is fixed in the two central holes, and a crank handle is attached to the projecting part in front. Each factory possesses several such cylinders, and their number depends upon the size of the works. Up to the present time, these cylinders have been made of cast-iron, although clay seems to be just as good, and even more durable.

"The fire being lighted, the cylinder is charged with 12 to 15 kilogrammes of green ultramarine and closed. The stirrer is moved now and then, in order to heat the ultramarine uniformly. When the temperature has been raised to the point at which a small quantity of sulphur, projected through the upper opening, will become inflamed, the fire is moderated, so as not to increase the heat. Half a kilogramme of sulphur is then charged in, the stirrer is revolved, and the upper opening is left open to admit the air necessary for the combustion of the sulphur. Afterwards, the stirrer is revolved more slowly, until it is seen that all the sulphur is burned out. A sample of the powder, being taken out with a small iron spoon, appears of a bluish-green color. More sulphur is added, stirred, and burned as long as the intensity of color increases. When the maximum of intensity is reached, the pigment will lose its qualities if this treatment be longer continued. The powder is then scraped out into a sheet-iron box, which also receives the small quantities of material which fall during the operation. A new charge of green ultramarine is immediately put into the cylinder.

"In many localities, the last calcination is done according to the method we have just described, except that there is an immediate washing, grinding, drying, and sifting, before the ultramarine has become entirely blue. In this manner, the coloring is more uniform, because there are no more green specks inside or out.

"The blue calcined colors are ready for the market, when they have been washed, dried, and sifted.

"The intensity of the blue color depends on that of the green, but grinding generally diminishes the depth of the color. Light blues are sometimes produced in the course of manufacture, and these mixed with dark ones form the medium quality. But, most generally, the light-colored qualities are produced by the addition of white pigments.

"In the French method of calcination, muffles are used, that is, a furnace into which the flame of the fireplace does not penetrate. Fig. 56 is a longitudinal section of a furnace of that kind, Fig. 57 a transverse section, and Fig. 58 a horizontal section at the level of the bed of the muffle.

Fig. 56.

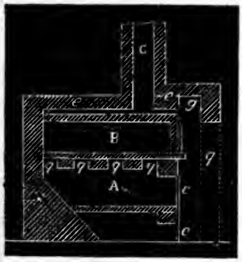


Fig. 57.

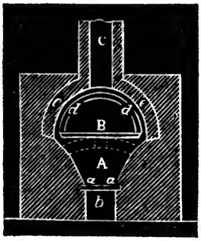
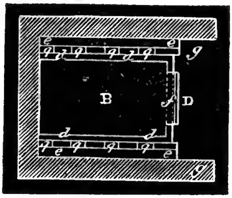


Fig. 58.



"The fireplace A is placed under the bed B, which rests upon a low arch. Several flues, *q q q*, conduct the flame into the space left between the dome *d d* of the muffle, and the concentric arch *e e* of the furnace. C is the chimney. The fireplace A is composed of grate bars *a a*, an ash-pit *b*, and doors *c c*. In front of the muffle there is an opening *f*, closed by a sliding-door D, which may be raised or lowered by means of a counter-weight and pulley. This opening is covered by an arched mantle *g g*, which conducts the sulphur fumes to the chimney, and prevents them from passing into the work-room. All the parts in direct contact with the fire are built of good fire-brick, cut and polished by friction upon each other. The number of muffle furnaces depends on the size of the works.

"The green ultramarine is evenly spread upon the bed, in layers 4 to 5 centimetres thick. The door is then closed, and the fire urged until the sulphur projected into the muffle becomes inflamed. A shovelfull of sulphur is charged in, and stirred with an iron hook, the door being raised just enough to allow of the motion of the hook. After the combustion of this sulphur, and an examination of a sample, a new quantity of sulphur is charged in, stirred, and so on, until the consecutive samples show no improvement in the purity and intensity of the color. No greater heat is required than that necessary for the sulphur to catch fire as soon as it is put in.

"The transformation of green ultramarine into blue is more rapid with this mode of operation, than with the cylinders, because there is greater access of the air, and therefore more sulphurous acid produced, and less volatilization of sulphur. As soon as the ultramarine has acquired the desired color, it is raked out into a sheet-iron box placed under the door. The furnace is charged again, and the operation progresses as before. We have already indicated the further treatment of the color.

"When ultramarine blue is washed by the process of displacement, there are obtained quite concentrated solutions of sulphate of soda, which may be utilized after precipitating by lime the iron contained therein.

"Ultramarine increases in weight by its combination with sulphur, and the increase, after washing the product, may amount to several hundredths. If the washings have not been thorough, the ultramarine will form compact masses in the packing barrels."

In further researches upon ultramarine, Mr. J. G. Gentele has ascertained that ultramarine green, boiled for a long time with a solution of sal ammoniac, and then transformed into blue ultramarine, possesses a purer color and a lesser greenish tinge than any of the ultramarines which have not been treated in this manner.

He concludes from these experiments, that sal ammoniac (and probably gaseous and dry hydrochloric acid) is the most remarkable bluing agent of ultramarine green, because, even employed in great excess, it does not act upon the ultramarine blue already formed.

L. *Fürstenau Process.*

The old methods of manufacturing ultramarine, such as have been introduced into the majority of the South German works, and are still retained in certain localities, are so inconvenient, especially when great quantities of a given product are to be prepared, that many attempts have been made to modify them.

Several Rheinish manufacturers have devised the preparation of ultramarine in a large reverberatory furnace, the bed of which is first heated below, and then above, by the returning flame. These furnaces contain enough material to produce about 600 kilogrammes of ultramarine, but their construction is such that the calcination is not regular and uniform, and that the substances are not protected against impurities.

This consideration has determined Mr. C. Fürstenau to propose another method, which seems to obviate all the inconveniences named, and which allows of the treatment of large quantities of material without the introduction of dust and impurities. At the same time the success of the operation does not depend on the men so much as before.

The ultramarine is calcined in fire-clay boxes, which may hold from 300 to 350 kilogrammes of material, and which are located on each side of a double reverberatory furnace, resembling a smalt furnace, but with a lower fireplace.

This furnace is composed of two stories A and B, the lower one being heated by the direct heat of the fireplace, and the upper one by the hot gases of the combustion. The internal chimney, the arch, and the bed of the first story are built of fire-bricks; ordinary bricks are employed for the second story; the pillars and outside work are of stone. The bed of the upper story A is covered with cast-iron plates, in order to avoid the wear and tear resulting from the introduction and removal of the calcining boxes. The boxes themselves are made of fire-clay slabs, 25 millimetres thick, with joints rabbeted and luted with clay. All of these joints are strengthened externally, in order to possess the required firmness.

The composition for dark alum ultramarine is as follows:—

Kaolin, slightly calcined . .	100	parts in weight.
Calcined soda ash (95°) . .	90	" "
Refined roll sulphur . . .	100	" "
Colophony	6	" "
Dry pine charcoal . . .	4	" "

Each of these substances, with the exception of the colophony, is reduced to a fine powder in revolving barrels by means of cannon balls. These barrels or tuns are of beech wood, a little over 1 metre in length, 0.65 metre at the largest diameter, and 0.55 in diameter at the ends. The staves are from 20 to 30 millimetres thick. These tuns are closed like those used for amalgamating, and the aperture is 13 to 14 centimetres in diameter, with a felt packing for preventing the escape of the powder.

The cannon balls employed are from 7 to 8 centimetres in diameter, and about 18 kilogrammes of them are introduced into each tun. The velocity is equal to 36 revolutions per minute.

As soon as the materials have become sufficiently comminuted they are mixed with colophony, broken into pieces of the size of walnuts, and the mixture is made to rotate for four hours more. The resulting grayish powder is placed, without packing it tight, in the fire-clay boxes. These are closed, and then introduced into the furnace. When all the apertures of the furnace have been luted, the fire is urged to bring the temperature as rapidly as possible to the melting point of an alloy composed of equal parts of gold and silver. This temperature is kept up for five to six hours, and the fire is watched by an opening left in the cleaning flue. In order to ascertain the state of the composition, there is a small clay pipe, 25 millimetres in diameter in the clear, one end of which penetrates the calcining box, while the other end projects about 5 centimetres from the furnace wall. Samples are taken now and then with a small iron spoon passed through this pipe, and resembling, on a smaller scale, the tools used for removing the powder from blast holes. If, after cooling, these samples become green, the fire is allowed gradually to die out, the chimney-damper is closed, and the furnace is permitted to cool off for twenty-eight hours.

After two days the bluish-green mass is extracted from the boxes, ground under vertical stones, and still more finely comminuted in revolving tuns. The powder is then charged in cast-iron boxes, 45 centimetres high, having a length of 65 centimetres on top and 55 on the bottom, and a width of 55 centimetres on top and 50 on the bottom. The thickness of the metal is 5 millimetres. These boxes are well closed with iron covers, and then introduced before the fire is begun, into the upper part of the furnace, which may contain nine of them; they remain there until twelve hours after the fire is run down. This mode of oxidation and of desulphurization is imitated from the mode of oxidizing red lead, and may be repeated without impairing the color.

The blue thus obtained is carefully washed and finely ground in water under horizontal quartz or granite stones. The revolving stone is in perfect equilibrium, and the surfaces of the two stones should be polished by grinding a mixture of sand and clay in water. The lower stone is tightly inclosed within a kind of ring, which rises 10 centimetres above the top of the upper stone, and which is closed with a cover. The circumference of the upper stone is provided with two inclined bands of sheet iron, which scoop the pigment and bring it on top, in order to pass again between the two grinding surfaces. With a revolving stone 1 metre in diameter, the velocity is fifteen revolutions per minute. A charge is composed of 25 kilogrammes of powder plus the quantity of water necessary. As soon as the color has acquired the desired brightness and firmness, which point is ascertained by examining a dried sample, the paste is received and drained in cloth bags, and then dried in cast-iron pots, placed in the upper portion of the furnace after the calcining boxes have been removed. The dry color is sifted and packed for the market.

M. *White Utramarine.*

Notwithstanding the researches of Gmelin, Tiremon, Weger, Pruckner, Winterfeld, Brunner, Dippel, Buchner, Habich, and Gentele, we see that there still exists a great deal of incertitude relative to the composition and mode of formation of artificial ultramarine. More recently, Mr. H. Ritter, of Lünebourg, has tried to throw some light on this subject, and he has made known the results of his experiments in a work published at Gœttingen, in 1860, under the title of *Uber das Ultramarin*, which should be consulted by all persons interested in this manufacture.

The most interesting part of the work of Mr. Ritter is the discovery of a white ultramarine produced at a temperature of 900 to 950° C., which demonstrates that the sulphide of iron is not the coloring principle of ultramarine, either green or blue.

This white ultramarine, which is easily transformed into green and blue ultramarine, is composed of—

Silica	39.66
Alumina	31.17
Soda	14.75
Potassa	1.60
Sulphide of sodium	8.09
Bisulphide of sodium	4.88
Sulphide of iron	0.11
	100.26

The experiments of Mr. Ritter have been published through extracts in the *Technologiste*, vol. xxii., No. for March, 1861. They are too extensive to reproduce here, and we shall, therefore, give only the conclusions of the work.

1. The combination, which takes place during the calcination of the sulphide of sodium and the silicate of alumina, is colorless; it is formed of silicate of soda, silicate of alumina, and a monosulphide, with a small proportion of polysulphide of sodium; but it contains no oxidized combinations of sulphur.

2. If a portion of the sodium be removed (by chlorine or sulphurous acid, for instance) from the sulphide of sodium of white ultramarine, the proportion of sulphur corresponding to this eliminated sodium combines with the remaining sulphide of sodium and forms a polysulphide.

3. The white ultramarine thus transformed becomes ultramarine blue by the absorption of oxygen, that is, by an oxidized combination of sulphur with a portion of the sulphide of sodium. This blue ultramarine is a combination of silicate of soda, silicate of alumina, a polysulphide of sodium, and a soda salt with an acid from the sulphur.

4. The sulphide of potassium, calcined with silicate of alumina, does not form a combination similar to that of ultramarine, but there results only a silicate of alumina and potassa without sulphur.

5. Moreover, it is very probable that the oxidized combination of sulphur, held in blue ultramarine, is a hyposulphite or a sulphite of soda, and the former hypothesis seems the more likely.

N. *Trial and Analysis of Ultramarines.*

I. Mr. Guimet has proposed the following manner of comparing ultramarines:—

"I weigh," says he, "a decigramme of each sample of ultramarine to be tried, and as many times 6 decigrammes of white as there are samples of ultramarine. The white I use is the best quality of Meudon white (chalk), which I keep in a bottle large enough to hold material for 1000 trials.

"I then mix upon a white marble slab, or, more simply, upon a piece of smooth and well-sized paper, 1 decigramme of blue and 6 decigrammes of white. This operation is effected rapidly by using a flexible painter's knife, with which the blue and white are crushed and mixed, until the whole presents to the eye no difference of coloration.

"Let us now suppose that we have made four mixtures, having each a different degree of coloration; it is evident that the ultramarine which has produced the greatest intensity of coloration is the richest and the most valuable.

"Taking now the darkest and the lightest samples, I try, by successive additions of white, to render the tone of the dark one equal to that of the light one; and if I have had to use 6 decigrammes more of white, I conclude that the blue, which bears twice as much white to produce the same azure tone, is twice as rich in coloring power, and twice as valuable in money value.

"I have chosen a simple ratio to render my reasoning more clear; but we understand that this trial will give us very approximately the relative values of blues.

"Sensible scales are necessary for weighing 1 decigramme; but with ordinary scales, the weight of the samples may be increased. For instance, we may take 1 gramme of blue and 6 grammes of white; the only inconvenience is that the mixing is a little longer.

"It results from the above stated facts, that ultramarine blues have a value in a direct ratio to their coloring power. This property is generally due to the fineness of the pigment. A great degree of comminution is always advantageous, but it is absolutely necessary for artistic painting and calico printing. On that account, I prepare special qualities for these uses, although I pay a great deal of attention to the grinding of all my blues.

"The results agree with what I have said, since the paper manufacturers prefer my blue to all others, even at a higher price. Most of my production is thus sold, especially in foreign countries.

"Calico printers want bright and very finely ground blues; my dark quality is generally preferred, since it is better fixed upon the cloth, and does not scratch the printing rollers."

II. Ultramarine, says Mr. J. P. Dippel, is distinguished from all the other blue pigments by its external appearance, especially by its soft qualities, and the intensity and purity of its color.

A simple process for distinguishing ultramarine from other pigments which resemble it, Thénard or cobalt blue for instance, consists in moistening the sample with hydrochloric acid. Ultramarine is entirely decolorized, and there is produced sulphuretted hydrogen, which is easily recognized by its smell.

An addition of indigo is detected by heating, and this substance emits purple vapors. Mountain blue becomes greenish, and lastly black, by heat. Prussian blue becomes brown when heated, or boiled with a solution of caustic potassa. Smalt and cobalt blue preserve their color in acids.

A good ultramarine should be of a dark-blue color, without grit and foreign admixtures. Ground with oil, it should not be decolorized by being heated in a crucible, or upon a red-hot piece of iron. It should also dissolve in concentrated acids without effervescence.

In order to determine the value of ultramarines, pieces of paper are colored with the different samples, and the tones of color are compared. While the ultramarine is mixed with a solution of glue or gum, if we observe a red or brown substance of a dirty color on the surface of the liquor, this ultramarine contains an excess of sulphide of sodium, which will change its color when used.

As it is possible that pipe-clay has been added to the ultramarine during the bluing calcination, in order to obtain light tones of color, the darkest kinds should generally be preferred. However, we should remark that there are ultramarines which, by an energetic calcination, have acquired more durability, but which are lighter colored. These are in no way inferior to the dark kinds.

III. Mr. C. P. Prückner, chemist and manufacturer at Hof, has found a process for determining the quality and durability of ultramarines, by a treatment with hydrogen. This gas, at a certain temperature, removes the sulphur from the ultramarine, and renders it reddish. Therefore, by heating the ultramarine in a glass tube, connected with a hydrogen generator, and passing the gas through, this chemist has obtained the following results with several samples of ultramarine at his disposal:—

1. *Artificial ultramarine of the first quality* (No. 0).—This ultramarine began to turn reddish, and after *half an hour* the blue color had entirely disappeared and passed to a greenish-gray.

2. *Inferior qualities.*—The inferior qualities of artificial ultramarine lose their color more rapidly. The No. 5 of Nuremberg manufacture was decolorized after *a few minutes*, and became a grayish-white.

3. A sample bought at Venice by Mr. Prückner, and certified to have been prepared from broken pieces of lapis lazuli, was submitted to the same treatment. After *one hour*, its color was still sensibly blue.

4. A sample of a remarkably fine native ultramarine, left in 1805 (at which time no artificial ultramarine was manufactured) in the corner of a pharmacy as a useless substance, was treated in the same manner. After *two hours* of contact with hydrogen gas in a hot tube, all the color was not destroyed.

"It results from these observations," Mr. Prückner adds, "that artificial ultramarine treated by hydrogen behaves differently from real native ultramarine prepared from lazulite, and it is probable that a similar result will be observed in painting. A similar example is found in cinnabar; the product prepared by the wet way presenting properties entirely different from the cinnabar produced by the dry way, or sublimed, when it is employed in the manufacture of wafers and sealing wax. The former especially, when colored by cinnabar (vermilion) prepared by the wet process, are more blackish-red than intensely red. The same effect is seen with sealing wax, although the vermilion (wet way) is brighter than that which has been sublimed.

"Generally speaking, the durability of color of ultramarine is influenced by the fixity of the substances entering into its composition, and by the intensity of the calcination. Repeated heatings in closed vessels increase the durability of ultramarine, but they are always accompanied by a diminution in the intensity of the color, which may become a pale blue. By this process, the ultramarine acquires such a durability that acids do not destroy this pale blue color."

IV. Mr. W. Büchner has made a special study of the practical testing of artificial ultramarines. The following is his mode of operation:—

(*a.*) *Resistance to the action of alum.*—As there is no ultramarine which will completely resist for a long time a hot and saturated solution of alum, we must, for those kinds of tests, remain within the limits of technical operations, and draw conclusions only after check-tests have been made with different ultramarines. The length of time required for the action of an alum solution upon ultramarine is an important consideration, and requires comparative trials. We should here remark, that a coarse-grained ultramarine resists the action of alum better than an ordinary ultramarine; it is not, however, suitable for paper manufacturers and calico printers, on account of its feeble coloring power, and the coarseness of its grain.

Such experiments require, 1st, a saturated and cold solution of alum; 2d, a few test glasses; 3d, a delicate scale; 4th, a graduated burette.

Five centigrammes of the ultramarine to be tested are weighed carefully, and placed in a glass, which is marked with a suitable sign or number, when comparative experiments are going on at the same time. Then an accurately measured volume of the cold and saturated alum solution is poured upon the color, and the whole is stirred with a glass rod. After a few minutes, several hours, or several days, we may see how the destruction of the ultramarine color progresses, and its degree of resistance. An ultramarine which with an equal coloring power resists the longer, is evidently the better. The reaction may be rendered more rapid by immersing all the test glasses in the same vessel holding hot water. If we consider that in the manufacture of paper, the pulp becomes sensibly heated during the work, this last experiment shows why we should prefer an ultramarine which resists the action of alum. But in order to arrive at a still more technical conclusion, we may, instead of a pure alum solution, employ a solution of glue in which alum is added. By cooling, the ultramarine remains suspended in the jelley, and the action is more energetic.

(*b.*) *Trial of the coloring power.*—The aspect of a color, whether dark or clear, is the result of the refraction of light, and it is well known that colors appearing alike may possess a coloring power widely different. In order easily to ascertain the difference, it is necessary to dilute the color with a powdered white body. The apparatus, etc., consist of a delicate pair of scales, a mixing dish, and a certain quantity of lenzinite,* sulphate of baryta, or white lead. One gramme of lenzinite and five centigrammes of ultramarine are carefully mixed in the dish, but without

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* Lenzinite is a kind of white clay, found in scattered lumps near Kall, in the Eifeld.

grinding. The other samples are worked in the same manner, and when the comparison is made, it is often a subject of astonishment to see the difference in coloring power of certain kinds of ultramarine. It is, of course, necessary that these experiments should be made with scrupulous exactness, and an unpractised eye may cause great mistakes. The mixtures are placed one near the other, or one upon the other, and they are slightly compressed with the spatula. Or they may be put into glasses with equal volumes of water. The distinction should be made only when the difference in tint or hue is perfectly apparent. The hue may sometimes be a pale blue, or a greenish-blue, or a reddish-blue, or a pink blue. But the most intense color will always be recognized.

It now remains to be seen which of these kinds are the best. It seems proven that the pure blue red qualities are the best for paper manufacturers, calico printers, and paint grinders, and that the greenish-blue ones are more advantageous for fancy papers.

For a long time, I had the idea to express the coloring power as is done in estimating the power of alcohol, bleaching powder, etc., by a scale, but we have no unit upon which to base ourselves, and, if for ultramarine a scale were to be constructed from the best sample, this same sample should be in the hands of all those who make similar tests. In order to render the operation possible, I have under the name of *ultramarinometer* (*ultramarinomesser*), adopted a normal or standard color, the mixture of which with any kind of white substances, gives the degree of the scale.

Any person having a few grammes of this color, or an ultramarine of the same coloring power, may determine the coloring power of any sample, with the following table:—

Scale of the Ultramarinometer.

2 grammes	of lenzinite with	0.5	gramme of	ultramarine give	10°	of coloring	power.
"	"	0.3	"	"	9	"	"
"	"	0.2	"	"	8	"	"
"	"	0.1	"	"	7	"	"
"	"	0.05	"	"	6	"	"
"	"	0.03	"	"	5	"	"
"	"	0.02	"	"	4	"	"
"	"	0 01	"	"	3	"	"
"	"	0.005	"	"	2	"	"
"	"	0.003	"	"	1	"	"

When the above scale has been prepared, 2 grammes of lenzinite are mixed with 0.5 gramme of ultramarine, and the mixture is compared with those of the scale. That with which the tested mixture agrees the best gives the degree of the coloring power of the sample of ultramarine.

(*c.*) *Trial of the printing power.*—A substance suitable for printing should be finely comminuted and require little thickening. The degree of fineness may be ascertained with a magnifying glass, or by rubbing the powder with the finger upon a piece of writing paper. If the substance contains coarse portions, and is not fine and homogeneous, it will be perceived by the sense of feeling. If no coarse grains are felt, and if, after striking the paper from underneath, a notable portion of the ultramarine remains adhering to the paper, this ultramarine appears to answer the purpose. A pinch of this powder is also rubbed against a polished piece of brass, which should not be scratched by it. But the best proof is that of the coloring power, because when it is high the degree of comminution must, of course, be satisfactory, taking however into consideration the accidental impurities which are often to be found.

(*d.*) *Trial of the glazing power.*—The property in ultramarine of acquiring a glaze is an advantage sought for in many of its applications. This property supposes a great fineness of body, a high coloring power, and the necessity of but a small amount of size. A single coat of glue size upon paper will enable us to ascertain this property. If, after this size has become dry, a glaze be obtained by a few strokes of a soft brush, then the ultramarine is satisfactory, because, in the manufacture of glazed papers, there is always added a small quantity of wax soap in order to aid the fixing of the printing colors. Such a result will be more readily obtained by using a wax soap, or brushes charged with powdered talc; but even with these means no ultramarine will glaze well if it does not do so without them.

(*e.*) *Trial for the proportion of gelatine* (*size*).—However simple such a problem appears, it cannot be solved except by a practical trial. A lean and common ultramarine will always require a great deal of glue, and, even with a good glue, its adherence will soon be defective. A small quantitative test may be made as follows: A certain quantity of ultramarine and glue is weighed, and the latter, after solution in water, is put into a graduated vessel. Then by adding this solution to the blue by small quantities at a time, and reading the number of divisions left after the proper result is obtained, we know the proportion employed. The sizing should be such that no ultramarine will be removed when the paper thus colored is dry and is rubbed with another piece of white paper.

It is well known that moderate prices increase the consumption of a product considerably, and the employment of ultramarine will attain enormous proportions when it shall be possible to obtain it at a low price. On the other hand, when the selling price is scarcely above the cost, the manufacturer is weighed down and cannot undertake improvements. The applications are therefore limited on account of the imperfection or of the inferior quality of the product. In regard to ultramarine, the comparison of the prices of different manufacturers will never be satisfactory if the color of the product be alone considered; because it is a well-known fact that two kinds of ultramarine, similar in appearance, may be different in their coloring power, and vary in price as 100 does to 200, independently of the other properties. Therefore, if we desire to establish comparisons of prices, it is absolutely necessary that we should take into account the intimate properties of ultramarine in order to arrive at its real value.

V. Mr. Barreswill has indicated the following process for ascertaining, very approximately, the value of ultramarine:—

An artificial sulphate of baryta is prepared by decomposing a solution of nitrate of baryta, or of chloride of barium, with sulphuric acid. The precipitate is well washed and dried. Two small mortars receive each 20 grammes of sulphate of baryta; on the other hand from 0.5 to 1 gramme of ultramarine is weighed in two porcelain dishes of a known weight. One of these dishes contains the standard ultramarine, and the other the sample to be compared. A certain proportion of the standard blue is then mixed with the sulphate of baryta, and small portions of the tested sample are added to the baryta of the other mortar, until the two tints have the same intensity. Weighing now the ultramarines left in both dishes, the differences of weight give the comparative value desired.

Ultramarine is sometimes adulterated with starch, which is easily detected by a tincture of iodine. The blue ashes are recognized by throwing a pinch of the suspected sample into aqua ammonia; pure ultramarine produces no change, whereas the blue ashes are dissolved and color the liquor an intense blue.

O. *Composition of ultramarines.*

The blue and green ultramarines have been analyzed by several chemists, who, from all the results of their analyses, have put forth theoretical views which have not yet resolved the problem of their composition.

Those persons who may be interested in these questions will find in the *Répertoire de Chimie pure et appliquée*, November, 1861, p. 420, an excellent *résumé*, made by Mr. A. Scheurer-Kestner, of the opinions of Messrs. Elsner, Brunner, Stœltzel, Breunlin, Gentele, Wilkens, Ritter, Bœckmann, etc. These opinions often disagree, and appear to have been recently overthrown by an experiment of Mr. E. Guignet, who has extracted, by means of bisulphide of carbon, notable proportions of sulphur from various samples of ultramarine, without decomposing the blue or changing its intensity. Artificial ultramarines, therefore, contain free sulphur, and the differences in coloration, durability, etc., of these blues may possibly be explained by the greater or less proportion of that sulphur. The greenish tinge of certain blues, printed with albumen, and then submitted to the action of steam, may possibly be caused by the presence of more or less free sulphur.

At all events the observation of Mr. Guignet is of great practical importance, and will possibly permit of the manufacturers changing their formulæ, or their mode of operation, in order to prepare durable products of a fixed composition.

3d. *Cobalt ultramarine.*

Cobalt ultramarine, or Gahn's ultramarine, from the name of the inventor, is a combination of alumina with the oxide of cobalt. This combination does not appear to be in definite proportions, since it varies with the different works in which this pigment is made.

Its preparation consists in making a solution of alum, that is, a double sulphate of alumina and potassa (or ammonia), and dissolving in it a certain proportion of nitrate, sulphate, or chloride of cobalt. The whole is then precipitated by another solution of carbonate of soda or potassa. The resulting abundant and pink-white precipitate is a mixture of carbonate of cobalt and of hydrated alumina, which is carefully washed with hot water, dried, and calcined in a crucible at a high temperature. After cooling, the product is ground into a fine powder which resembles the blue ultramarine of the first quality, but appears violet under artificial light. By varying the proportions of cobalt more or less intense tones of blue will be obtained. If a great purity of color be desired the materials employed should not contain iron.

Cobalt ultramarine unites quite well with other pigments used in oil painting, and is scarcely poisonous.

§ 12. *Blue ashes. Lime blue. Copper blue. Mountain blue.*

The composition of this color, which is of a sky blue, has been a secret for a long time. It was imported from London, and was prepared with the copper resulting from the treatment of silver bullion. Pelletier was the first chemist who, after having analyzed a sample of fine English blue ashes, succeeded in preparing them in France. In order to obtain blue ashes of a constantly fine quality, it is necessary, according to this chemist: 1. To mix powdered lime with a weak solution of nitrate of copper ($CuO.NO^5$), and to employ these substances in such proportions that all of the lime is saturated by the nitric acid, that is, by keeping always a certain excess of undecomposed nitrate of copper; 2. To wash the precipitate several times; 3. To drain it upon a cloth; 4. To grind it with 7 to 10 per cent of its weight of lime; 5. To dry it.

This process, described by Pelletier, is not that followed by manufacturers. It appears that the latter obtain the blue ashes by pouring a solution of commercial potash into one of sulphate of copper, washing the precipitated carbonate of copper, and grinding it with lime, to which a small proportion of sal ammoniac has been added. This salt, being decomposed by the lime, increases the brightness of the color, with which it forms a kind of ammonium compound of a deep blue.

Another blue ash, called arseniate of copper, is obtained by dissolving 5 kilogrammes of arseniate of potassa in 32 litres of hot water, and pouring into it another solution of 3.5 kilogrammes of sulphate of copper. The precipitate is washed with water, then drained upon a cloth, and dried in the shade.

Blue ashes with size are often employed for theatrical decorations and painted papers. They present the inconvenience of turning green after a few days, especially when they are exposed to the action of solar light. Ground in oil, they become dark, and lose part of their beauty. Those made in England, of which we shall explain the preparation, are more durable. When blue ashes are ground upon a slab with a muller, they feel very greasy, but afterwards they become much more fluid.

I. *Manufacture of the ashes in England.*—We have already seen that the nitrate of copper, resulting from the parting of silver, is generally used; but it appears that any soluble copper salt, the acid of which will make a soluble salt with lime, is just as convenient. Therefore, the cheap sulphate of copper may be first decomposed by the acetate of lead or the acetate of lime, and, in some localities, by the chloride of calcium.

We should observe that, if we cannot, by this double decomposition, accomplish the combining of exactly the whole of the sulphuric acid with the lime (which, however, is not difficult after a few trials), it is preferable to have a small excess of sulphate of copper in the liquor rather than one of lime salt.

The solution of copper resulting from this double decomposition should contain but a very small proportion of sulphate of lime. It is filtered, after having settled in a cool place for at least 24 hours.

The filtered solution is diluted with pure water until its specific gravity becomes about 18° Bé.

On one hand, a milk of lime is prepared with very white and well-burned lime, which is slaked and mixed with a large quantity of pure water. The milk is kept stirred for a long time in a lead-lined tun, having a stopcock at a few centimetres above the bottom. After one minute given for the settling of the sand and other impurities, the milk of lime is drawn out through the stopcock, and is then allowed to settle entirely in other vessels lined with lead, or in copper pans. When the deposit has acquired a certain consistency, it is ground in a mill similar to those employed for indigo, mustard, enamels, etc., and which should contain no iron. The axis is of hard bronze or brass. The lime should be ground long enough to destroy any hard and coarse portions, and, as a further security, it is passed through a very fine copper sieve.

As the mixture of lime and copper solution must be made in certain proportions, the quantity of dry material in the copper liquor and in the milk of lime is determined by drying samples of them. This test is made, for instance, upon 1 litre of the solution of copper, and the same volume of milk of lime; but the latter should be well stirred before taking the sample. The proportions for mixing are 1 part of well-dried lime, and 1.75 parts of dry copper salt. We should observe that the quantity of lime may be considerably increased above this proportion at the expense, however, of a lesser intensity in the coloration of the product. The proportions which we have just indicated generally furnish the finest color. In order to ascertain whether the correct amount of lime has been added, a sample of the clear liquor above the colored precipitate is tried with ammonia, which should produce but a faint blue. If the coloration be deep, more milk of lime is added, and the whole is thoroughly mixed.

When the precipitate has become well settled, the clear liquor is decanted, and the color is carefully washed with pure and limpid water. It is then drained upon cloth filters until it has acquired a certain consistency, and forms a green paste.

For the subsequent operations, it is necessary to determine the proportion of water held in this green paste, in order to compound the ingredients. A few grammes are slowly and cautiously dried, and the loss in weight indicates the proportion of water. This paste generally loses three-fourths of its weight in drying. On this hypothesis 25 kilogrammes of paste are stirred, in a leaden tub, with 50 litres of pure water, to which are added 2.5 kilogrammes of the wet lime, which are immediately stirred without loss of time, this rapidity being an essential condition. Afterwards, 1.5 litres of a solution of the best kind of pearlash potash, marking 15° Bé., and filtered clear, are added, and immediately and vigorously stirred in. The mixture is then carried, without loss of time, to the mill already mentioned, in which it is ground for a long time, because the beauty of the pigment depends greatly upon a homogeneous mixture.

On the other hand, for the 50 litres of green paste there has been prepared a clear solution of 0.5 kilogramme of pure sal ammoniac in 10 litres of water, and another solution of 1 kilogramme of sulphate of copper in 10 litres of water.

The liquid paste of the mill is then drawn into a stoneware jar, and, immediately after, the two solutions of sal ammoniac and sulphate of copper are poured in at the same time. The jar is closed with a good cork, which is held tight by a string, and luted over with a mastic of tallow and rosin, soft enough to yield to the fingers. The jar is moved in every direction and shaken as much as possible.

After standing for four or five days, the contents of the jar are poured into a lead-lined tub of a capacity of about 250 litres. Water is added up to a few centimetres from the top, the whole is stirred, then left to settle, and the clear liquid decanted, and so on, at least eight times. The clear water of the last washing is tried with a piece of turmeric paper, and, if the yellow color becomes brown-red, the washing should be continued.

The deposit thus obtained is called, in England, *verditer in paste.* The greater portion of that manufactured is used in that state by manufacturers of paper hangings. For other arts, and for exportation, the paste is slowly dried, and becomes solid and brittle.

This manufacture requires great cleanliness, well-ventilated rooms, no sulphuretted gases, etc. Pure waters have a great influence on the beauty of the product.

II. A skilful manfacturing chemist, Mr. L. G. Gentele, has published, in the *Technologiste*, vol. xvii. page 341, the results of researches made by himself upon the preparation of several copper colors, and especially of blue ashes.

"The blue colors," says he, "found in the trade, and prepared especially with oxide of copper, are: The mountain blue, the green-blue of Bremen, and the calcareous blue, or blue ashes in paste. As far as I know, no accurate researches on the latter product have been published; and the circumstances under which it is formed are so peculiar, that I suspect that colors made in a similar manner may be compounds in chemical proportions.

"One kind of blue ashes in paste is obtained by the precipitation of sulphate of copper with a very thin milk of lime added in excess, and cold, and by thoroughly washing the precipitate, which may then be dried without turning black. The preparation of another kind of blue ashes in paste, resembling mountain blue, is made by precipitating, in the cold, a solution of 100 parts of sulphate of copper and 12.5 parts of sal ammoniac with a milk of lime prepared from 30 parts of quicklime. The liquor remains blue for a few days, and when this coloration has disappeared the pigment is made. In order to obtain very pure colors the lime is ground after having been slaked, and the milk of lime formed is left to stand for several weeks before it is employed.

"As the latter color is not obtained without sal ammoniac, I have concluded that this substance is of absolute necessity in its preparation. I have, therefore, prepared a solution of ammoniacal sulphate of copper with excess of ammonia, that is, I have added ammonia in sufficient quantity to dissolve the first precipitate, and to impart a strong ammoniacal odor to the solution, which was filtered afterwards in order to separate a small quantity of oxide of iron.

"By pouring, drop by drop, this solution into lime-water, I have immediately obtained a blue precipitate, and the liquor took a bluish coloration only when all of the lime was combined. The precipitate formed before the coloration of the liquor was separated and washed; then a portion A was dried and kept to be analyzed.

"If, on the other hand, the milk of lime be poured, drop by drop, into the ammoniacal copper solution, there is also produced a precipitate, which by stirring is completely redissolved, and remains so for a long time, when the liquor is tepid. Lastly, when a permanent precipitate has been formed, and has been separated by filtration, the liquor, after standing for several days, deposits crystals of a magnificent blue, several centimetres in length, but no thicker than a hair, which break into small pieces when the liquid is stirred. These crystals B were separated in order to be analyzed.

"The compound A was not entirely pure, on account of the presence of a small proportion of carbonate of lime, formed during the washings and drying. This product greatly resembles Bremen blue, except that it is slightly greenish, flaky, and amorphous. Under the action of heat, it behaves like the hydrated oxide of copper of the Bremen blue, but it bears a greater elevation of temperature before it becomes brown.

"The analysis made of it gave as result—

Water	18.76
Sulphuric acid	11.20
Oxide of copper	46.85
Lime	16.19
Loss	7.00
	100.00

"The loss consists of carbonic acid. The proportion of lime, not combined with sulphuric acid, requires 6.5 of carbonic acid. Therefore the analysis becomes—

$$\left\{\begin{array}{l}11.20 \text{ sulphuric acid,}\\ 7.84 \text{ lime,}\end{array}\right.$$

$$\left\{\begin{array}{l}8.35 \text{ lime,}\\ 6.50 \text{ carbonic acid,}\end{array}\right.$$

46.85 oxide of copper,
18.76 water.

"This precipitate, thoroughly washed in pure water, became very soluble in ammonia, whereas, previous to the washings, it was insoluble. We should therefore suppose that this precipitate, before being dried and washed, holds a combination of lime, which, during the drying operation, combines with carbonic acid, and sets at liberty the hydrated oxide of copper. As the washings carry away the sulphate of lime, it is difficult to decide upon the composition of the precipitate.

"The compound B may be obtained pure in the shape of crystals, or rather of a crystalline precipitate. It is generally impure in commercial blue ashes in paste. This blue is very bright, and resists the action of the air well. The thicker crystals possess the blue color of mountain blue, although slightly lighter in tone. Heated, these crystals acquire a brown color, of a glassy brightness. They are insoluble in water, but very soluble in the sulphate of ammonia.

"Their analysis gives the following composition:—

Lime	16.19	
Oxide of copper	33.56	33.44
Sulphuric acid	23.83	
Water	26.01	27.00
	99.59	

"This compound is not obtained by digesting sulphate of lime with ammoniacal sulphate of copper containing an excess of ammonia.

"From the behavior of caustic lime with ammoniacal sulphate of copper, and also from the differences presented by the two precipitates, we may establish rules for the method of preparing this color, and foresee the circumstances which will influence its good or bad quality. For instance, the compound B is not formed, when the proportion of lime is such as to precipitate entirely the sulphuric acid of the sulphate of copper. Out of 7 atoms of sulphate of copper in the liquor, 5 are precipitated by hydrated lime, and the last two are decomposed by ammonia. A greater proportion of lime will produce a precipitate holding a certain quantity of the compound A, which is less valuable, and impairs the quality of the color. A smaller proportion of lime renders the color finer and more crystalline, because it crystallizes partly in the excess of solution. It is therefore possible, by an incomplete decomposition and a smaller yield, to obtain a finer and more crystalline color.

"If we calculate the proportions necessary for the formation of the color, we have—

7 equivalents of sulphate of copper;
2 " " ammonia;
5 " " lime.

And if, instead of 2 equivalents of ammonia, we take 2 equivalents of sal ammoniac and 2 of lime, the weights become—

100 parts of sulphate of copper;
24 " " lime;
22.5 " " sal ammoniac,

which proportions will furnish the purest color.

"Examination has also been made as to how a solution of ammoniacal sulphate of copper, with excess of ammonia, behaves with caustic potassa or soda. Either of these alkalies produces in this solution a fine blue precipitate, but the liquor does not become decolorized, except by evaporating the ammonia. By washing this precipitate, its color becomes lighter and lighter, and finally resembles that of Bremen blue.

It is composed of hydrated oxide of copper, but it contains also a small proportion of carbonic acid.

"It is a remarkable fact that this precipitate, even when heated in the presence of a great excess of potassa or soda, does not become brown, as is the case when a solution of sulphate of copper is precipitated by a slight excess of these bases.

"The presence of ammonia renders the hydrated oxide of copper much more durable. This circumstance explains a useful manipulation in the preparation of Bremen blue. Indeed, if, for changing to a blue the precipitate obtained from a copper salt by an alkali which is not entirely caustic, we employ a caustic lye of potassa with an addition of ammonia or of sal ammoniac, we are much more certain of success, because a passage to a black color, which is to be feared, does not then occur even with a great excess of caustic potassa lye."

III. Since blue ashes are manufactured in England better than in France, it is necessary to be able to distinguish one from the other. The following process has been proposed:—

When the blue ashes are in paste, a sample is thoroughly dried at a low temperature, and then heated in a glass tube with a small quantity of fused caustic potassa or soda. The French blue ashes disengage ammonia, easily recognized by its smell, while the English product does not present the same phenomenon.

The English blue ashes, the manufacture of which is still kept a secret, are a carbonate of copper of a rather dark blue, but less pure in color than the hydrated oxide of copper of Mr. Peligot.

IV. The natural color, called *mountain blue*, *azurite*, and *Armenian stone*, is a basic carbonate of copper, found in quartz rocks in Siberia, the Tyrol, Bohemia, Saxony, Hesse, England, and France. This substance is rare and expensive, and possesses a very rich sky-blue color, of which blue ashes are an imitation. The native product is always more durable than the artificial one.

§ 13. *Smalt.*

Smalt, which is also known under the names of *azure blue, smalt blue, zaffer blue, Saxony blue, enamel blue, starch blue, cobalt glass*, etc., appears to be, according to Mr. Ludwig, a double silicate of potassa and cobalt, mixed with variable quantities of lime, alumina, magnesia, oxide of iron, oxide of nickel, and sometimes of arsenic and carbonic acid, and water. The intensity of the color, in the opinion of the same chemist, depends on the greater or less proportion of the double silicate.

The crude materials employed in the manufacture of smalt are, cobalt ore, sand, and potassa. The mineral generally used in Saxony, where this color is prepared the best, is a speiss or arsenide of cobalt and iron.

The broken ore is roasted at a red heat in a reverberatory furnace, which has a very high stack for carrying far up into the air the arsenical and sulphurous fumes. When vapors cease to be disengaged, and when the material begins to be pasty, the roasted product is removed from the fire, cooled, pulverized, and passed through a silk sieve. This powder is called *zaffer*.

A pure sand free from iron, mica, talc, or lime, is also calcined and thrown into cold water, while still red-hot. It is then powdered, washed with hydrochloric acid, and dried.

The potassa should be pure, and contain no lime, sand, or chloride of sodium.

It is difficult to indicate beforehand the proportions for the mixture, because we must be guided by the nature of the cobalt ore, or by the quality, or by the tone of color which is to be produced. The cobalt and sand are first added, and then the potassa; the whole is introduced into clay pots having each a hole in the bottom, which may be closed. The pots are then placed in a glass furnace heated by a wood fire. After four, five, or six hours of calcination, the material is melted, and forms three layers; the upper one, or dross, is composed of sulphate and arseniate of potassa, and chloride of potassium; the lowest one is composed of ore and of unmelted substances, and the intermediary one is the blue glass.

The greater part of the dross is taken off with hot iron ladles, and the lowest layer of unmelted materials is removed through the bottom hole. After this hole has been closed again, the melted blue glass is ladled out into basins filled with cold water. The pots are charged again, and a new operation begins.

The glass is removed from the water, dried, and pulverized under horizontal stones. The powder is then levigated (floated), in order to obtain various degrees of fineness, which are designated by the names of smalt of the first, second, third, and fourth fire, or by other marks distinctive of their color or degree of comminution.

Independently of the ordinary smalt, there is another darker blue, with a very fine grain, and which is generally called *Eschel blue* or *Laundry blue.* It is obtained by mixing finely powdered zaffer with a smalt of good quality. It is distinguished from the real smalt by stirring it in water; after a few seconds, the zaffer is precipitated, whilst the smalt remains in suspension in the liquid.

In order to obtain a smalt of a magnificent blue, it should be prepared with a pure oxide of cobalt. The ore is finely ground, and treated by boiling nitric acid, which makes nitrates of cobalt and of iron, and arsenic acid. The liquor is decanted, diluted with water, and decomposed by a solution of carbonate of soda. There is produced a soluble arseniate of soda, and a precipitate of the carbonates of cobalt and iron, which is collected, carefully washed, dried, and then calcined. The resulting oxide of cobalt, holding a small proportion of oxide of iron, is mixed with sand and potassa.

The smalts of Saxony, most generally found in the market, are marked with the following letters, of which F, M, and O indicate the proportion of cobalt, and C, CB the degree of fineness of the grain:—

H,	Common smalt.
E,	Eschel variety.
B,	Bohemian smalt.
CF,	Fundamental color.
FC,	Fine color.
FCB,	Fine color from Bohemia.
FE,	Fine Eschel.
MC,	Medium color.
MCB,	Medium color from Bohemia.
ME,	Medium Eschel.
OC,	Ordinary color.
OCB,	Ordinary color from Bohemia.
OE,	Ordinary Eschel.

In order to indicate a smalt which contains more cobalt than F, several F's are added; thus FFFC is of a higher price than FFC, and this is more valuable than FC. On the other hand, if the blue contains less cobalt than OC, ordinary color, a number is employed; thus OC^2, OC^3, indicate that the smalt contains one-half or one-third of the cobalt of the ordinary quality.

If azure blue be employed for inside painting, it has the inconvenience of turning green and black; moreover, the difficulty of grinding it fine enough prevents its employment for artistic painting. Its principal use is for giving an azure color to signs, for instance, which are painted with ordinary blue oil paint, and then dusted over with the smalt. It changes less in size than in oil, and on that account is much used in fresco painting. It dries rapidly.

§ 14. *Cœruleum.*

Cœruleum is a new blue color for oil and water painting, which is due to the English house of G. Rowney & Co. It is a light blue, slightly greenish, and does not appear violet under artificial light. It covers very well, it is not granular, and is especially well suited for painting a transparent sky blue.

Cœruleum is not altered by solar light or an impure atmosphere, and caustic alkalies and strong acids are without action upon it at the ordinary temperature. According to Mr. S. Bleekrode, it belongs to the colors with a basis of cobalt oxide, although it is distinct from the silicate of cobalt and potassa or soda, as Mr. Ludwig calls smalt blue, or from the aluminate of cobalt of Gahn, the cobalt ultramarine of Binder, and the phosphate of alumina and cobalt of Thénard.

Cœruleum is entirely soluble in hot hydrochloric acid, and the light-blue coloration of the solution becomes a violet red when it is diluted with water. The primitive color reappears by concentration, and the pigment is restored if the solution be evaporated to dryness. Nitric acid dissolves the cobalt and leaves a white residue, which is mostly composed of stannic acid. The green coloration of this solution shows the presence of a small proportion of iron and nickel. Concentrated sulphuric acid does not dissolve cœruleum; but the same acid, diluted with 4 volumes of water, produces a partial decomposition. Acetic acid and caustic potassa do not act upon it at the temperature of ebullition.

Cœruleum is principally a combination of an oxide of tin with the oxide of cobalt. The greenish-blue reaction by which oxide of tin is recognized with the blowpipe is generally known. Berzelius mentions a stannate of cobalt, which he prepares by adding a solution of stannate of potassa to one of cobalt. The bluish precipitate thus formed becomes of a light-red color after washing, and then brown. If it be calcined at a white heat, its color is changed into a light blue.

The composition of cœruleum is—

Oxide of tin (stannic acid)	49.66
Oxide of cobalt	18.66
Sulphate of lime and silica	31.68
	100.00

The stannate of cobalt of formula $SnO^2.CoO$ requires 75 parts of stannic acid, and 37.5 parts of oxide of cobalt; the ratio is therefore as 2 : 1. The formula of cœruleum is, therefore, $3(SnO^2.CoO) +$

SnO^2, that is, a stannate of cobalt mixed with stannic acid and sulphate of lime.

It is said that there is in the market an imitation of cœruleum, prepared by mixing French ultramarine with a small proportion of Naples yellow and white lead.

§ 15. *Litmus.*

This coloring substance is manufactured in Auvergne, Dauphiné, Holland, etc., from several lichens, especially the *Variolaria orcina* of Achard. The process consists in grinding them, and making a paste with urine and half of their weight of crude potash. Care is taken to replace the evaporated urine. After 40 days of putrefaction the mixture acquires a purple color. It is then put into another trough, with urine, and the blue color is developed. The paste is afterwards mixed with lime and urine. The last preparation consists in giving a certain consistency to the paste, by the addition of carbonate of lime, and moulding the mixture into small cubes, which are dried.

Litmus is used only in distemper painting, or for giving an azure color to ceilings. It is often preferred for violet and lilac body grounds, on account of its hue. This color is not durable, and becomes red by the action of acids. It becomes violet with glue size, and black with oil.

§ 16. *English sky blue.*

Although this blue has little to do with painting, we think that the two following processes may be profitably given, since the products are largely used in the household, and manufacturers of colors should know how to prepare them. The following formula has been given by W. Story: Take a large glass vessel, or an iron kettle (but in the latter case it is not necessary to use iron filings), and put into it 1 kilogramme of fine indigo in powder, and 3 kilogrammes of sulphuric acid at 66° Bé.; stir, and let stand for 24 hours, at most.

On the other hand, dissolve 10 kilogrammes of potash in 20 litres of water, and pour 2 litres of this solution into the indigo mixture, and stir well. Afterwards add 1 kilogramme of finely-cut blue (Castile) soap, stir continually, and add the solution of potassa until the whole appears as a dry powder(?). Pour on then 1 litre of pure water and the remainder of the potash solution. Lastly, mix 0.5 kilogramme of finely powdered alum. After standing for three days, the mixture is made into balls, which are dried in the air, and employed for bluing linens.

Balls of Wuy.

Indigo	1 kilogramme.
Sulphuric acid at 67° Bé.	6 kilogrammes.
White potash	15 "
White soap	1 kilogramme.
Quicklime	100 grammes.
Common salt	100 "

The powdered indigo is purified in 10 litres of alcohol, then in dilute hydrochloric acid, and after drying in the shade or in a moderately hot stove-room, is ground again very fine. It is then dissolved in sulphuric acid, and the solution is poured into a lead-lined vessel, in which the other ingredients are added. When the paste is thick enough it is moulded into balls.

SECTION III.

YELLOW COLORS.

Yellows in general.—Yellow pigments are derived from many substances, some of them being natural, and the others artificial products. It is to be regretted that the light and bright tones of yellow are often wanting in fastness and durability. Iron, antimony, lead, chromium, arsenic, cadmium, and several vegetable substances, such as weld, quercitron bark, Persian and Avignon berries, yellow wood, curcuma, saffron, and ahoua, are the raw materials used at the present time for the manufacture of yellows. *Yellow ochre, Rut ochre, raw Italian earth, raw Sienna earth, and Mars yellow* are iron compounds. *Naples yellow, mineral yellow, chrome yellow, Cologne yellow, Turner yellow, mineral gamboge, antimony yellow, orpin, massicot,* etc., are artificial colors manufactured from antimony, lead, chromium, and arsenic. Lastly, *Avignon berries, terra-merita, saffron yellow, stil de grain, and weld yellows, those from quercitron bark, and yellow wood,* are extracted from various vegetable substances.

§ 1. *Ochres.*

This is the name given to various clays, the paste of which is more or less fine, smooth, opaque, dull, easily broken, adhering to the tongue, and, when wet, emitting a peculiar clayish smell. Those of good quality are greasy to the touch and are easily ground. On the other hand, those which are dry and sandy are more difficult to grind, and are, therefore, less esteemed.

Ochres are colored *brown, yellow, red,* and *reddish-*

yellow; nevertheless we put them together under the same head, because, by calcination, they all become *red* or *brown.* The good qualities of ochres are in direct ratio with the number of washings or floatings they have been submitted to. Their color is due to the oxides of iron they contain. In fact, ochres are compounds of clay and oxide of iron.

Yellow ochre, more or less pure, is a true yellow, but earthy looking. There are many varieties of it, and it will be sufficient to give as examples the two following, which are well fitted for painting.

I. *Ochre from Saint-Georges-sur-la-Prée* (Cher). It is composed of—

Clay	69.5
Peroxide of iron	23.5
Water	7.0
	100.0

It is of a handsome yellow, of very fine grain.

II. *Ochre from la Berjaterie* (Nièvre). Its composition is—

Clay	64.4
Peroxide of iron	26.6
Water	9.0
	100.0

Its color is as deep as the preceding one, but not so finely granulated. Very good ochres are also extracted from Pourrain, Diges, and Toucy (Yonne).

When yellow ochre is calcined, water escapes, and the substance becomes red. It is then *red ochre.*

For removing the water from the hydrated oxide of iron, and, at the same time, causing the red coloration to appear, the yellow ochre is broken into small pieces which are calcined upon a plate of cast-iron, heated from below. When the substance has acquired the desired tone of color, it is quickly cooled by being thrown into water. After several washings the deposit is dried in the open air. The greater the proportion of iron, the brighter the ochre; but we must suppose that the clay contains no organic substances capable of reducing the metal.

Ochres are not generally sold as they are extracted from their beds, but are dried in the sun, pulverized, and sifted to a greater or less degree of fineness as desired by the trade. For still finer ochres, they are ground in a mill, and floated in large cisterns. The longer the time required for the ochre to subside, the finer its quality. The deposits are collected, dried in the sun, and sold powdered or in lumps.

It has been attempted to manufacture ochres of various degrees of fineness, by submitting the powder to a powerful blast of air in rooms or troughs of great size. The greater the comminution, the greater the distance the powder is carried away. By collecting the products in the order in which they have settled, we obtain ochres of every degree of fineness.

The yellow ochres are generally sold in powder or in lumps; but the red ochres, called *Prussian red*, *brown-red*, *red earth*, and *Nuremberg red*, are sold in the powdered state, whereas the retailers deliver them in the form of paste. It is sufficient to grind the red ochres with a small proportion of water and of chloride of calcium. This salt, on account of its hygrometric properties, maintains a certain dampness in the paste.

Mr. Cochois calcines his ochres in perfectly tight ovens, or in closed iron vessels. The product is then washed for the purpose of removing the foreign substances. The tones and hues may be varied at will by calcination.

Mr. de Rostaing, as we have already seen in the articles on white lead, has invented a process for pulverizing fused metals by centrifugal force. With cast-iron, it seems possible to produce very cheaply oxides and iron colors for painting. But this process has not been applied on a large scale.

Pure yellow ochre with glue size, or oil, acquires the color of gingerbread, and is used for painting stone floors. Mixed with red ochre and a white pigment, it produces the various tones of wood and stone. The mixture with black is olive-green.

§ 2. *Rut (rivulet) ochre.*

This ochre is a hydrate of sesquioxide of iron, mixed with clay and silica. It is generally found in the rivulets in the vicinity of iron mines. Its color is brownish-yellow, and it forms earthy and pulverulent masses. Its tone becomes darker with glue size, and with oil it resembles chocolate. Mixed with from 10 to 12 times its own weight of white lead, it has the color of oak wood.

This ochre is composed of—

Sesquioxide of iron	83
Silica	5
Water	12
	100

§ 3. *Italian and Sienna earths.*

Italian earth resembles in tone of color Rut ochre, but is brighter. On the other hand, *Sienna earth* is neither so bright nor so fast; indeed it is more easily changed by many foreign substances. In their raw state, these earths are brown-yellow with an orange tinge; calcined, they are of a fine brown-red. All these natural raw ochres, used for ordinary and distemper painting, necessitate no other preparation but their thorough washing and floating in water in order to allow the foreign substances to settle down and be separated. The washed pigment is collected upon paper filters held upon stretched cloths, and when it has become sufficiently dry, it is formed into troches which are completely dried upon other gray blotting papers.

§ 4. *Venice red. Antwerp red. Terra rosa.*

There are to be found in the trade, under the names of *Venice red*, *Antwerp red*, and *terra rosa*, other ochres which have very likely been prepared in the same manner as ordinary red and yellow ochres.

Venice red is a splendid red ochre which comes from Italy; but its preparation and the exact place from which it is extracted, are not well known.

Antwerp red is a fine ochre which is exported from Flanders.

Lastly, terra rosa is an Italian ochre, which is lilac-red when in powder, and deep red when ground in oil. It would be extensively used in the arts were it better known, and to be had in larger quantities.

§ 5. *Mars yellows.*

Whatever be the care taken in the preparation of ochres, they always have an earthy look, which prevents them from being used in fine painting. The effort has been made in the arts to manufacture a product having the same durability as ochres, but purer, and of a brighter color. The best known process for this purpose is that of Mr. Bourgeois, and is as follows:—

Sulphate of iron is prepared by dissolving an excess of clean wrought iron in sulphuric acid diluted with 4 or 5 parts of water. The crystallized sulphate is dissolved in pure water, and an equal quantity of a solution of alum is mixed with it, and poured into a pine tub to about 1 centimetre above the bottom. The tub is then filled with pure water which has not been filtered upon charcoal, because it may contain carbonic acid, which will alter the oxide of iron. The mixture is precipitated by a solution of American potash. After a thorough stirring and settling for 24 hours, the water is decanted, and the precipitate collected with a wooden spatula. After draining upon paper, the deposit is formed into troches, which are allowed to dry upon blotting paper.

This preparation, which is supposed to be a mixture of hydrated oxide of iron, carbonate of iron, and alumina in variable proportions, is of a fine gold-brown yellow. If it be calcined at different temperatures, and under particular conditions which are held secret, the product is an iron or Mars violet, red, brown, and orange. It is probable that during these operations the oxide of iron, mixed with alumina, becomes more or less peroxidized and dehydrated.

As the Mars yellow is quite expensive, and requires a great deal of practice for its successful manufacture, the effort has been made to substitute other preparations for it, such as a mixture of sulphate of lime and oxide of iron made as follows:—

One kilogramme of protosulphate of iron (green copperas) is dissolved in 20 litres of water, and into this solution is poured a sifted milk of lime, prepared by diluting in 40 litres of cold water one kilogramme of very white quicklime. A green precipitate is thus formed, which is washed several times with cold water, and then exposed to the air. It soon becomes peroxidized, and acquires a yellow tinge.

A reddish-yellow is also prepared by precipitating a solution of sulphate of sesquioxide of iron with carbonate of soda. The deposit of hydrated sesquioxide is washed, but its color is never pure. Part of the reddish tinge may be removed by adding a small proportion of alum.

The artificial ochre (oxide of iron and alumina) is a good substitute for the natural ochres; it is of a gold brown-yellow, and, when mixed with white lead, many tones and hues may be obtained, which are very fine and durable.

The various tones and hues of natural ochres are due to foreign matters, which it is very difficult and expensive to separate. On the contrary, the combinations of Mars yellow with other fast colors allow of the production of all the desired colors and hues, which possess great durability.

§ 6. *Curcuma or terra merita.*

This root is also known under the names of *Souchet, Indian saffron, Curcuma rotunda,* and *C. longa* (Lin.), according as it is round or elongated. These two kinds come from the East Indies, and differ but slightly. The elongated one is more commonly found in the trade, and is cylindrical, twisted, nearly as thick as the little finger, and orange-yellow inside. Its fracture resembles wax, the thin envelope is like shagreen, its taste is hot and bitter, and the smell is analogous to that of ginger.

The round curcuma forms ovoid tubercles, nearly as big as English walnuts, and, when newly gathered, united with filaments. The envelope is gray, and presents many circular rings. The properties of this curcuma are the same as those of the preceding one. Berthollet once examined a sample of curcuma from Tabago, and found it superior to that generally met in the trade, not only as to the size of its roots, but also in the greater proportion of its coloring principle.

This substance is of a deep color, and no other yellow is brighter, but it is not lasting (fast). Common salt and sal ammoniac are the best mordants to fix this color, although they darken it towards a brown. A small proportion of hydrochloric acid is also recommended. The best roots are very fragrant, heavy, compact, and saffron-yellow. Their quality is best judged when fresh and whole, although they are employed dry and powdered. Painters use curcuma for painting floors.

From an analysis by Vogel and Pelletier, the composition of curcuma is—

Yellow coloring matter, or curcumin,
Brown " "
Substance analogous to extracts,
Lignin,
Amylaceous fecula,
Gum in small proportions,
Bitter and fragrant volatile oil,
Chloride of sodium.

It is with ether that is extracted the neutral substance of a splendid yellow color, although not very fast, which is called curcumin.

In order to give more durability and greater depth to the orange-yellow color of curcuma, it is often mixed with Avignon berries and carthamus.

§ 7. *Stil-de-grain.*

Stil-de-grain is a lake prepared with the buckthorn of the dyers (*Rhamnus infectorius*, Lin.), the berries of which contain a yellow coloring substance, called rhamnin, which turns deep yellow with alum, and yellowish-brown with alkaline carbonates.

The berries of the buckthorn which grows at Avignon, in France, are called *Avignon berries* even in Spain and Italy. They are generally preferred on account of their cheapness, although the proportion of coloring principle is greater in those grown in the East, and which are known by the names of *Persian berries, Andrinople berries, Turkey and Morea berries.* These fruits or berries are small, of a yellowish-green, with two or three united shells or envelopes. Their smell is strong and nauseous, and their taste bitter and disagreeable. They blacken by age, and their quality deteriorates. They are gathered before complete ripeness, and give a fine yellow without fastness.

Stil-de-grain is prepared by boiling for one hour, 1 kilogramme of berries in 8 litres of water, and passing the decoction through a sieve. The berries remaining upon the sieve are again boiled in 4 litres of water. This second decoction is also passed through the sieve and mixed with the first. The liquors are then filtered, and 1 kilogramme of powdered alum dissolved in them. When cold, the alumina is precipitated with carbonate of soda, and carries with it the coloring matter, which will be the darker as less alum is employed.

Another process.—The berries are gathered before maturity, then bruised and put into a kettle with 4 to 5 parts of water and $\frac{1}{5}$ of alum. The yellow liquor obtained after half an hour of ebullition is filtered and mixed with $\frac{1}{2}$ to $\frac{3}{4}$ of a part of very white and fine chalk, which has been stirred in a small quantity of water and passed through a fine sieve. After stirring and settling, the liquor is decanted, and the precipitate is washed and drained upon a frame. When it has acquired the proper consistency it is divided into troches which are dried at a low temperature.

The color which is sold as stil-de-grain is not always prepared exclusively with Avignon berries; it is quite customary to boil the berries with variable quantities of weld (woad), quercitron bark, curcuma, yellow wood, etc., and to add to the solution holding alum, potash, or chalk, until all the coloring principle is precipitated. In such case proceed as follows:—

Boil 250 grammes of Avignon berries, 250 grammes of curcuma, and 180 grammes of carthamus, in 8 litres of water, and reduce to 6 litres; remove the kettle from the fire, and add 125 grammes of powdered sulphate of ammonia. The liquor being filtered through a cloth, and cooled off enough to allow of the fingers being held in, pour it slowly upon 1.5 kilogrammes of powdered Paris white, which is continuously stirred with a spatula.

Then throw the mixture upon a cloth fixed to a wooden frame, and pour back on top the filtering liquors until they pass clear and colorless.

The Paris white, which has become yellow upon the filter, is left there until it has acquired sufficient consistency to be divided into small lumps, which are allowed to dry thoroughly.

Stil-de-grain is a fine yellow color, without fastness. It is employed for painting scenery in theatres, floors, etc.

The coloring matter of Persian berries has been examined by Mr. Kane, who has extracted by means of ether a yellow substance called *chrysorhamnin.* This by boiling in water becomes oxidized and transformed into *xanthorhamnin.* Since then Mr. J. Ortlieb, chemist at Lille, has ascertained that the coloring principle of Persian berries is held in the state of glucosides, soluble in water. These glucosides may be split, either spontaneously or under the influence of acids, into sugar and coloring substances, which are—1. Gold-yellow granules of crystalline appearance, produced in a fermenting decoction, and called *rhamnin;* 2. Another coloring matter afterwards spontaneously deposited, and named *hydrate of rhamnin;* 3. Lastly, a product of transformation by the aid of sulphuric acid, the *hydrate of oxyrhamnin.* There is the same analogy between rhamnin and the hydrate of oxyrhamnin as between the chrysorhamnin and the xanthorhamnin of Mr. Kane. Oxyrhamnin is isomeric with euxantic acid, the coloring principle of Indian yellow.

§ 8. *Weld lake.*

Weld or Woad (*reseda luteola*) is a plant which contains several coloring principles in its leaves, stem, and seeds. Mr. Chevreul gives the name of *luteolin* to one of these principles, which is yellow, bright, and not easily altered by the air or dampness. It is soluble in water, and becomes under the action of potassa, soda, ammonia, lime, and baryta, of a deep-yellow color. Weld is used in the preparation of a lake, which is a compound of luteolin with alumina, or of luteolin with lime and alumina.

The weld is cut into small pieces, which are put into an enamelled or varnished pot with sufficient water to cover them. When the water is near the boiling point, a weight of alum equal to that of the weld is added and dissolved. After boiling for some time the liquor is filtered and precipitated with a solution of potash until the latter begins to dissolve part of the alumina, which is ascertained when the effervescence ceases. The whole is then thrown upon a filter and washed several times with hot water. The color is put into the shape of troches.

We find in an English paper the following process for extracting from weld a pure yellow in impalpable powder:—

Put about 2 kilogrammes of fine levigated chalk into a copper kettle with 2 kilogrammes of pure water. Boil, and stir with a spatula of white wood, until the chalk is thoroughly tempered. Add then for each kilogramme of chalk from 180 to 200 grammes of powdered alum. There is an effervescence produced, due to the disengagement of carbonic acid, and the contents of the kettle may run over if the addition of the alum is not gradual. When no more carbonic acid escapes, the kettle is removed from the fire.

Another kettle receives the weld, roots upwards, and enough water is poured in to cover all the parts of the plant which hold seeds. A quarter of an hour's boil is given, and the plants are removed, roots upwards, to a perforated tub, where they are allowed to drain. These drainings, mixed with the liquor of the kettle, are filtered through a funnel, and contain the coloring material.

There is no practical way of ascertaining exactly the proportion of weld corresponding to a given weight of chalk, since the quantity of seeds in a package of weld is variable. But should there be too much coloring matter prepared, it may be kept without decomposition, in stoneware or wooden vessels, for several weeks.

Heat again the kettle holding the aluminous precipitate, and pour into it the decoction of weld until the desired tone of color is reached. Then boil for a few minutes, when the operation is finished. In order to ascertain that the maximum of color is obtained, take now and then a small sample of the mixture, and put it upon a piece of chalk, where it will dry immediately. If then the pigment be spread with a brush upon a piece of white paper, it will be easy to judge of the depth of the color.

The contents of the kettle are poured into a stoneware or wooden vessel, where they are allowed to settle for twenty-four hours. The liquors being decanted, the deposit is spread over pieces of chalk, and dries rapidly.

The decanted liquors may be employed for a second boiling, adding the water necessary to make up the bulk. The plant itself may be boiled twice, and there is a certain saving of coloring matter by so doing.

We should avoid exposing this coloring substance to the contact of iron, which acts upon it.

Manufacturers of paper hangings consume the greater proportion of weld lake, two kinds of which are to be found in the trade: I. Superfine lake; II. Lake No. 1. It is to be regretted that this color is not fast, and on this account it is rarely employed for oil or water colors.

MM. P. Schutzenberger and A. Paraf have recently made the analysis of luteolin, the coloring principle of weld, and have found its composition to be—

Carbon	62.068
Hydrogen	3.448
Oxygen	34.484
	100.000

The chemical formula of luteolin, dried at 150° C., is, therefore, $C^{24}H^{8}O^{10}$; that of crystallized luteolin is $C^{24}H^{10}O^{12}.HO$.

By treating, at 200° C., luteolin with anhydrous phosphoric acid, we obtain a red substance which with ammonia makes a violet solution.

When luteolin is heated in sealed tubes with caustic ammonia, for three or four days, and at the temperature of 100° C., it becomes entirely dissolved, and the solution is of a deep-yellow. This liquor, being evaporated to dryness, leaves a dark residue called *luteolamide*, which does not disengage ammonia by a treatment with caustic lime. On the other hand, it produces ammonia with caustic potassa.

§ 9. *Lakes of quercitron and yellow wood.*

Quercitron, such as is found in the trade, is a fawn-colored powder mixed with fibrous portions, ground from the bark of an American oak (*quercus nigra*). This bark contains a yellow principle called *quercitrin*, which, viewed with a magnifying glass, appears of a light and slightly grayish-yellow. Alum-water changes it to a fine yellow. By processes similar to those employed with weld, it is possible to obtain from quercitron a lake, which is not, however, so handsome as that made from weld.

Yellow wood (*Morus tinctoria*) contains a coloring principle called, by Mr. Chevreul, *morin.* Alum, with a decoction of yellow wood, furnishes a canary-yellow precipitate. This wood may, therefore, be employed for the preparation of a yellow lake, which, however, in beauty and durability, is inferior to that of weld.

We shall examine, further on, new processes for the manufacture of vegetable lakes of a red color, and which may be applied to the preparation of yellow ones.

§ 10. *Chrome yellows.*

Chemistry and the arts are indebted to Vauquelin for the discovery of chromium, a peculiar metal which he found, in 1797, in a sample of Siberian red lead (chromate of lead). Vauquelin distinguished in the new metal the remarkable coloring power of its combinations; indeed, the name which he chose means color. Among the combinations of chromium those most employed in the arts are the chromates of lead, lime, and baryta. The neutral chromate of lead is of a very fine and bright yellow, which is used for printing on cloths and on porcelain, for paper hangings, and for house and carriage painting. All the other chromates have different colors, and Thénard believes that several of them will be employed for various colors and hues which cannot be obtained from other substances.

Since all the other chromates are prepared with chromate of potassa, we think it desirable that we should endeavor to cause its preparation to become well known.

One of the processes for the manufacture of this salt consists in calcining at a high temperature a mixture of nitrate of potassa and chrome ore, the latter being a compound of the oxides of chromium and iron, with some silica, alumina, and magnesia. The proportion of nitre is one-half, or, at most, two-thirds of the weight of the chrome ore when it is very hard. Should too great an excess of nitre be present, the earthy substances would be corroded by the alkali of the nitrate, and the chromate be rendered impure. The oxygen, disengaged from the nitre by heat, oxidizes the iron and acidifies the chromium. The chromate of potassa is freely soluble in water, and is separated by washing the calcined residuum. The insoluble portions still contain a certain proportion of undecomposed chrome ore.

Chromate of potassa is of a fine lemon-yellow color, crystallizes in prisms, and is composed of—

Chromic acid	100
Potassa	92.307

It is also known under the names of *neutral chromate* and *yellow chromate of potash.* There is another well-known salt, the bichromate of potassa, or acid chromate, which is of a handsome red color, and crystallizes in quadrangular prisms. It is less soluble in water than the neutral chromate, and contains twice as much coloring substance (chromic acid). Its composition is—

Chromic acid	100
Potassa	46.153

1. *Neutral Chromate of Lead.*

A neutral chromate of lead, of a very rich tone, will be obtained by dissolving, for instance, 10 kilogrammes of neutral chromate of potassa in 100 litres of hot water. We also dissolve in another vessel, 20 kilogrammes of neutral acetate of lead (sugar of lead) in 50 litres of water. When the solution of chromate of potassa is boiling, we carefully pour into it that of acetate of lead, and allow the precipitate to settle. This latter is washed several times by decantation, drained upon cloth filters, and dried in a stove-room. There should remain a small excess of chromate of potassa in the liquor, in order to prevent the formation of a basic chromate of lead, which will impair the light yellow of the neutral chromate.

If we substitute nitrate of lead for the acetate, the product will be still brighter. The proportions will then be, forty-two parts of nitrate of lead, and nineteen parts of bichromate of potassa. The composition of the neutral yellow chromate of lead is—

Chromic acid	31.71
Oxide of lead	68.29
	100.00

Baron Liebig has indicated another process for the manufacture of a very dense neutral chromate of lead:—

The sulphate of lead, left as a cheap secondary product in dye works, is digested and stirred in a warm solution of neutral chromate of potassa. A double decomposition takes place, by which a soluble sulphate of potassa and an insoluble chromate of lead are formed. The liquors are decanted, and the precipitate is washed, drained, divided into square prisms, and dried in a stove-room at the temperature of 50° C.

This chromate is cheaper, and quite as fine as the preceding one, although it is more dense and does not cover so well. It generally contains a certain proportion of undecomposed sulphate of lead.

Neutral chromate of lead possesses great body, and a fine yellow color, the tones of which vary considerably with different manufacturers. It can be had from a light yellow to an orange-red, and these differences are due to the mode of preparation.

2. *Basic Chromate of Lead.*

This yellow, known in the trade under the names of *gold yellow* or *orange paste*, possesses a reddish-yellow hue, which is quite pleasing. It is a combination of chromic acid with more oxide of lead than is contained in the neutral chromate.

The most economical process for preparing this basic chromate or chrome yellow consists in boiling, for one hour at most, fifteen parts of chromate of lead with two parts of caustic lime fused in a small proportion of water. By the reaction which takes place, a soluble chromate of lime is formed, and the remaining basic chromate of lead is washed, drained, dried, and heated in a crucible until the desired hue is obtained.

We may also treat three parts of neutral chromate of lead by two parts of oxide of lead. Or, a solution of acetate of lead may be poured into another boiling solution of chromate of potassa, holding an excess of caustic potassa or soda. The precipitate resembles vermilion.

A basic chromate of lead is prepared by boiling, for several hours, equal weights of white lead and chromate of potassa. There is formed a soluble carbonate of potassa, and a basic chromate of lead, which is heated in a crucible until it acquires a scarlet color.

Lastly, if we melt in a crucible nitrate of potassa, and add dry and powdered chromate of lead by small quantities at a time, there is a production of red nitrous fumes, of chromate of potassa, and of basic chromate of lead, which latter sinks to the bottom. The chromate of potassa is poured out while it is still hot, and the crucible is left to cool off. The chromate of lead is removed, washed several times, drained, and dried in a stove-room. Its color is cinnabar red.

The trade furnishes a quantity of basic chromates of lead, with hues varying from a reddish-yellow to a vermilion-red.

Mr. Mérimée asserts that alumina, added to inferior qualities of chromates, preserves their brightness.

It is probable that the variations in hue and tone are often due to small proportions of sulphate of lead, and of chromates of lime, baryta, and alumina, almost always found in chromates of lead.

3. *Jonquil Chrome Yellow of Winterfeld.*

The jonquil chrome yellow of Mr. Winterfeld is a basic chromate of lead which is not calcined. Therefore, the oxide of lead is hydrated. It is prepared as follows:—

Dissolve 33 parts of acetate of lead in 100 parts of pure water, and filter. The clear liquor is kept in a vessel of sufficient capacity to hold about twice that volume of liquid.

In another vessel dissolve 22 parts of crystallized carbonate of soda in 60 parts of pure water, and filter.

The soda solution is then slowly poured, stirring all the while, into that of acetate of lead, and there results a white precipitate which is allowed to settle. The supernatant liquor is a solution of acetate of soda.

During these operations, another solution has been prepared with 17.15 parts of neutral chromate of potassa in 50 parts of water. It is poured upon the precipitate of carbonate of lead, and the stirring is continued until all of the chromate of potassa is decomposed, that is, until the clear liquor is no longer colored yellow.

The chrome yellow thus obtained is washed with pure water, drained upon a filter, pressed, and then cut into blocks and dried. The product is 27 parts of chrome yellow, from the proportions indicated above.

The jonquil chrome yellow of Winterfeld is the lighter in color, as the proportion of acetate of lead is greater.

4. *Cologne Yellow.*

This yellow is obtained by decomposing sulphate of lime and chromate of lead with a solution of soda.

Another way is to have very finely powdered sulphate of lime kept floating in a solution of chromate of potassa, and to precipitate with neutral acetate of lead.

This color is very bright and fast, and is used for distemper painting. It is a compound of chrome yellow with the sulphates of lime and lead.

Troches of this yellow, analyzed by Mr. Boutron-Chartard, had the following composition:—

Sulphate of lime	60
Sulphate of lead	15
Chromate of lead	25
	100

Chrome yellows are in great demand for oil painting, on account of their brightness and durability. Moreover, mixed with vermilion, they give chamois hues; with white lead, straw yellow and jonquil;

with Prussian blue, magnificent greens, which are not, however, lasting.

Since these pigments possess great intensity or coloring power, they are often adulterated with sulphate of lime, chalk, white lead, sulphate of lead, starch, etc. Several of these substances, however, cannot be considered as fraudulent mixtures because they result from the mode of preparation itself, or have been added to arrive at a desired tone of color. Nevertheless, as the manipulations necessary for ascertaining the foreign substances are quite complicated, we advise the consumer not to make the analysis himself, but to entrust it to the hands of an experienced chemist.

5. *Chromate of Lime.*

If we pour chromate of potassa into a solution of chloride of calcium, nitrate of lime, or other soluble lime salt, we obtain a precipitate of chromate of lime, which is of a fine straw-yellow color, and is used in distemper painting. Its covering power is small, but it does not blacken like the chromates of lead.

In the manufacture of chromate of lime the solutions employed are—one of bichromate of potassa saturated with carbonate of soda, and one of chloride of calcium obtained by dissolving chalk in hydrochloric acid. The latter solution is slowly poured into the former, and the precipitate of chromate of lime is allowed to settle and is then drained, washed, and dried.

6. *Chromate of Baryta.*

A solution of bichromate of potassa is saturated with carbonate of soda, and, after evaporation and cooling, a double chromate of potassa and soda is obtained. On the other hand, carbonate of baryta is dissolved in hydrochloric acid, and the chloride of barium is made to crystallize. Two separate solutions are effected, one with 25 parts of the double chromate, and the other with 20 parts of chloride of barium; these are mixed cold, or better still, hot, and are kept well stirred. The precipitate is a fine lemon-yellow chromate of baryta.

This pigment is employed in the manufacture of paper hangings, and for adulterating chrome-yellows. It is open to the objection of darkening in the air, and is sometimes improperly called *ultramarine yellow*. We shall again examine the chromate of baryta further on.

We now introduce an extract from a memoir published by Mr. Habich in the *Technologiste*, vol. xviii. page 171, upon the manufacture of the neutral chrome yellow, the red or basic chromate, and the chrome green.

A. *Chrome Yellow.*

The manufacturers of chrome yellow, who distinguish themselves by the beauty of their products and by their skill in obtaining a given hue, says Mr. Habich, employ soluble lead salts. It is true that the sulphate of lead, obtained in large quantities in dye works, gives a cheaper chrome yellow; but its hue is not constantly the same, and it is far inferior in depth and brightness of color to other chrome yellows prepared by other processes. On the other hand, it appears to suit very well for certain green colors obtained by mixture, such as the green cinnabar, the chrome green, etc.

We have first to explain how to prepare a solution of lead.

Small wooden tubs, 45 to 50 centimetres high and 1 metre in diameter, are disposed one on top of the other, so that their contents may pass through a spigot at the bottom into the lower ones. Four such tubs are sufficient for the apparatus.

These tubs are filled with thin ribbons of lead prepared as follows: The molten lead is slowly poured, by means of an iron ladle, into water which is kept stirred with a broom. Practice will soon teach how to arrive at the greatest thinness of metal, the main points being to ascertain the proper height of the ladle above the surface of the water and the thickness of the stream of molten lead.

When all the tubs are charged with lead the spigots are closed, and the upper tub is filled with strong alcohol vinegar, which should be, as far as practicable, free from the coloring and extractive matters, gum, sugar, etc. After a few minutes the spigot is opened in order to allow the liquor to run into the second tub, and afterwards into the third and the fourth. This first passage of the vinegar through these tubs dissolves but a slight proportion of lead. Indeed, this first operation simply consists in thoroughly wetting the metal, and aiding its further oxidation, which is seen to progress favorably when the lead becomes covered with a bluish-white pellicle. For dissolving the oxide of lead formed the first tub is again filled with vinegar. After half an hour the liquor of the first tub is emptied into the second, and so on until the solution is saturated with lead. It is then collected in a larger tub below. When the oxidation of the lead goes on rapidly, the saturated liquor contains a basic acetate of lead, which, by exposure to the carbonic acid of the air, is soon covered with a white film of carbonate of lead. For the manufacture of chrome yellow enough acetic acid is added to this solution for slightly reddening blue litmus paper. The liquor is then put into large settling tanks for the deposition of the impurities, and there should always be a good supply of it at hand.

Another tank also contains a stock of a solution of bichromate of potassa prepared as follows: 25 kilogrammes of this salt are dissolved in ten times their weight of hot water, in a copper kettle, and then poured into the tank with enough water to make about 5 hectolitres. Altogether 20 parts of water to 1 of bichromate of potassa.

In order to operate rapidly and with certainty, the following articles are needed: 1, a tub of white pine, 1.25 metres high, and of equal diameter, with several holes at different heights, and closed with plugs; 2, a small wooden tub, holding about 2 hectolitres, and provided with a spigot near the bottom; 3, two pails, holding each from 10 to 12 litres; 4, a graduated tube; 5, a barrel covered with a filter; 6, a wooden platform or tray edged all round.

Before beginning the operation it is necessary to ascertain the degree of concentration of the lead liquor, which depends on the very variable strength of the vinegar employed. Experimental tests are therefore applied, in order to ascertain how many volumes of the solution of lead are necessary to saturate ten volumes of the chromic solution, that is, to obtain after precipitation a liquor holding neither oxide of lead nor chromic acid.

Ten volumes of the solution of bichromate of potassa are measured in the graduated tube, and then poured into a tumbler, which also receives the water with which the tube is rinsed. The same tube is now filled with the lead solution, and the volume noted. It remains now to let the lead liquor fall into that of bichromate, drop by drop, as long as a precipitate takes place. The volume of lead solution poured out is marked down, and indicates the number of volumes of the stock of lead solution necessary to precipitate ten volumes of the liquor of bichromate.

For obtaining the various hues of chrome yellow there are several methods, which are based upon the chemical composition of the different yellows obtained from chromium. These compositions should therefore be carefully studied if we desire to operate with certainty.

When we precipitate a solution of lead by one of red bichromate (acid) or of yellow chromate (neutral) of potassa, the dark lemon-yellow precipitate is, in either case, a neutral chromate of lead, which has the same composition, that is, 112 parts of oxide of lead to 52 parts of chromic acid.

There is another combination called chrome red, and we shall see its preparation further on. It contains but one-half of the chromic acid of the neutral chromate, that is, 26 parts of acid to 112 parts of oxide of lead. If the chromic solution holds a certain quantity of free alkali, the latter separates from the lead solution a proportional amount of oxide of lead, which, mixing with chromate of lead, colors it red. If, therefore, we are enabled to prepare the mixtures with accuracy, it will be possible to produce all the desired tones and hues ranging from dark lemon-yellow to chrome-red. The process consists in adding a caustic lye of known strength to the washed precipitate of neutral chromate.

There are two double combinations of neutral chromate with sulphate of lead (Cologne-yellow) corresponding with the formulæ $PbO.CrO^3 + PbO.SO^3$ and $PbO.CrO^3+2PbO.SO^3$. The first takes place when a corresponding proportion of sulphuric acid is added to the chromic solution employed for precipitating the lead liquor. A solution, prepared as we have previously said, holds 2.6 kilogrammes of chromic acid per hectolitre, and requires 1.82 kilogramme of concentrated sulphuric acid. The precipitate, formed and collected upon a filter, increases in volume considerably. After drying, it is a very light pigment of a light lemon-yellow color, which is remarkably fine.

The second combination takes place when the proportion of sulphuric acid is 3.65 kilogrammes per hectolitre of chromic solution. It does not increase in volume as does the former article, but, after drying, the pigment is of a sulphur color, with a smooth fracture.

The first combination is employed especially for preparing ordinary chrome yellows, mixed with the sulphates of baryta, lime, etc., and is remarkable for its covering power. The second combination is particularly suitable for the bright greens resulting from the mixture of Prussian blue with chrome yellow.

Since the tones of color of these two combinations are so different, it is evident that by varying the proportion of sulphuric acid, it will be possible to obtain all the intermediate tones between light lemon yellow and sulphur yellow.

The success in the preparation of certain chrome yellows often depends upon the mode of working, which I shall now indicate.

For preparing the combination $PbO.CrO^3+PbO.$

SO^3, a tub is filled to two-thirds of its capacity with water, and then with the quantity of lead liquor necessary for decomposing 125 litres of chromic solution holding 6.25 kilogrammes of bichromate of potassa. This quantity of chromic solution is held in the small tub, and is mixed with 3.25 kilogrammes of sulphuric acid. This mixture is then allowed to run slowly into the lead solution, which is kept constantly stirred. After settling, the supernatant liquor, rich in acetic acid, is decanted, and the deposit is twice washed with water in the tub, before it is collected and drained upon a cloth. As soon as drained, the pulp is spread upon a wooden tray. These operations of washing and draining should be effected as rapidly as possible, in order that the pulp shall not swell on the cloth, but on the tray. Indeed, should the swelling take place upon the cloth, the pulp would become denser when spread upon the tray, and would thus lose a portion of that lightness which is so much sought for in it. When everything goes on without loss of time, the pulp is spread upon the trays, which are deposited in a cool place as long as the swelling continues, and until the paste has acquired consistency. The mass is then cut into large cubes, which are dried in the sun. Their crust is generally disfigured by the crystallization of a certain proportion of undecomposed chromate of potassa, which cannot be removed by the most thorough washing. This is made to disappear by means of a brush, taking care not to inhale the flying dust. The sweepings are kept for an inferior quality of yellow, or for the preparation of green cinnabar (chrome green).

The second sulphur yellow combination is obtained in the same manner, only that the proportion of sulphuric acid is double, that is, 6.5 kilogrammes per 125 litres of chromic liquor. The precipitate is rapidly washed, filtered, drained, and pressed. The cut blocks are dried in the shade in a well-ventilated room. If all these operations are not effected rapidly, it may happen that a slight admixture of the first combination will cause the pigment to swell up, and thus destroy the smooth and even fracture required by the trade.

B. *Chrome Red or Basic Chromate.*

Chrome red is another color, the preparation of which is nearly related to that of chrome yellow.

All the chrome reds, from the darkest cinnabar red to a minium red without lustre, are simply distinguished by the size of the crystals of their powder, and the observation may easily be made with a microscope. If various chrome reds of the same hue, but with different intensities of color, are reduced by grinding to the same degree of comminution, their powder will then possess the same intensity of coloration, but the brightness disappears.

Therefore, if chrome reds are desired very bright and intense in color, we should search for the conditions which aid in the formation of the crystals. One of the best processes consists in avoiding all agitation, which may prevent the formation of crystals or destroy them.

I recommend in that respect, the following method: Chrome yellow is precipitated in the usual manner, without sulphuric acid, and is washed carefully. After draining, the mass is well stirred, and six or eight equal samples are taken from it and put into glass vessels of the same size and thickness of material. Each sample receives a different volume of a caustic lye of potassa or soda, marking about 20° Bé. For instance, to 5 volumes of paste we add 2, 2½, 3, 3½, 4, 5, etc. volumes of lye. The different mixtures are thoroughly and rapidly stirred, but the chemical reaction is allowed to take place without any disturbance. After examination of the quality of the products, the relative proportions of pulp and lye* are noted down for the best hues of color. If there be a stock of lye of known strength, this experiment is sufficient to reproduce on a large scale the desired color.

The operation is then performed in a large tub, which receives the mixture of pulp and caustic lye in the proportions previously found. The changes in the color are soon perceived, and the reaction requires about twelve hours. After that length of time, the lye which has appropriated a great deal of chromic acid is decanted. The pigment is carefully washed with pure water once in the tub, and the mass is gently stirred. The washing is continued upon the filters, by throwing water upon the pulp, and in this manner there is less friction between the crystals which retain their deep color.

It is well understood that a very dark chrome red, which is highly crystalline, is not expected to possess great covering power.

C. *Greens by Mixtures* (*Cinnabar Green*, *Chrome Green*).

This branch of the manufacture of colors presents but few interesting facts.

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* Too considerable a proportion of caustic lye will fail to deepen the red color. Indeed, chrome red is entirely soluble in an excess of lye, and forms needle-like crystals, holding potassa, when the caustic solution has absorbed carbonic acid from the air.

Many manufacturers have tried, without success, to prepare a fine chrome green having a smooth fracture, by mixing Paris blue with pure chrome yellow. A good product will be obtained if a light chrome yellow with smooth fracture be employed, and if the mixture be compressed immediately after the addition of the blue.

A chrome green, with smooth fracture, may be prepared by an admixture of recently precipitated hydrate of alumina. A solution of 12 kilogrammes of alum (free from iron) in hot water, is decomposed by a clear lye of soda. The precipitate is washed and mixed with about 5 kilogrammes of finely ground sulphate of lime, 7 hectolitres of the above indicated chrome solution, and the required proportion of Prussian blue. The lead solution is then added.

For the manufacture of green cinnabar it is important to add a small proportion of indigo carmine, which gives great brightness and a bluish tinge. This is the best method for preparing that bright pigment called *silky green* or *seiden grün*; and in the manufacture of fancy papers, it has been customary for a long time, to increase the brightness of the coats of green cinnabar with a final coat of a solution of indigo carmine.

§ 11. *Various chromates.*

Chromate of zinc was first proposed as a yellow pigment by MM. Leclaire and Barruel. They gave it the name of *butter cup* (*bouton d'or*) *yellow*, and thus describe its preparation in the patent they have conjointly taken out:—

1. *Chromate of Zinc.*

"The chromate of zinc is a salt of which little is known. Very few authors mention it, and they do not agree as to its physical properties.

"From our researches, trials, and experiments, we have determined upon the following processes for preparing this salt:—

"1. The employment of a double salt of potassa and soda, that is, a double chromate of potassa and soda.

"2. The employment of a sulphate of zinc previously deprived of iron or copper salts, and made sufficiently neutral by ammonia, or better still, by carbonate of soda.

"3. The neutralization of the mother liquors and of the first washings of the chromate of zinc, by the carbonate of soda. This operation is necessary for finishing the preparation of the chromate.

"4. Utilizing the washings of the chromate of zinc for the production of a green which is fast and unalterable, by making sulphuretted hydrogen or sulphur act upon these hot mother liquors.

"We make upon a sand bath, and in stoneware vessels, a peculiar solution of a neutral chromate of soda and potassa.

"We should observe that this neutral chromate of soda and potassa is chosen on account of the economy in its manufacture. Indeed, the neutral chromate of potassa is more expensive than our double chromate, or than the bichromate of potassa, with which we prepare our double chromate by the following formula:—

"We take 100 kilogrammes of bichromate of potassa, which we powder and dissolve in hot water. We then add, by portions at a time, 95 kilogrammes of crystallized carbonate of soda, which is the equivalent proportion for obtaining a neutral double chromate of potassa and soda. The commercial sulphate of zinc is dissolved in three times its weight of water, in stoneware jars placed upon a sand bath. A stream of chlorine is then passed through the hot solution, and peroxidizes the iron salt present. There is also sometimes a certain proportion of sulphate of copper. When the solution has become turbid from a yellow and flaky precipitate of subsulphate of sesquioxide of iron, the stream of chlorine is interrupted, and a slight excess of oxide of zinc is added (about 5 per cent. of the sulphate of zinc).

"The liquor is made to boil, and the oxide of zinc takes the place of the copper and iron, which are precipitated. An equivalent proportion of sulphate of zinc is thus formed. As a test, a small quantity of the liquor is filtered, and a few drops of a solution of yellow prussiate of potassa are added to it. If the precipitate be white, there is enough of oxide of zinc; on the other hand, a precipitate which becomes bluish by the contact of the air shows the presence of iron, and the liquor is to be boiled again with a fresh addition of oxide of zinc.

"After ascertaining that the liquor no longer contains iron or copper, it is filtered into tubs having holes at different heights. Ammonia, or better still, carbonate of soda, is added until there is formed a slight precipitate of oxide or carbonate of zinc. This operation is absolutely necessary if we desire to obtain pulverulent chromate of zinc, of a fine yellow color, and if the mother liquor is to hold a minimum quantity of chromate of zinc and potassa. Without this precaution, and since the sulphate of zinc is always acid, there is formed a bichromate of potassa which does not react upon the sulphate of zinc.

"The proportions which we find to be the best in the preparation of the chromate of zinc are:—

"For the above indicated quantity of chromate of soda and potassa, we need 184.5 kilogrammes of sulphate of zinc. It is not possible to set down in advance the proportions of ammonia or carbonate of soda; they are added until there is formed a precipitate of oxide or of carbonate of zinc.

"The solution of double chromate is poured into that of zinc, as long as a precipitate takes place, and the mixture is kept stirred with a wooden board. After settling, the liquor is decanted and is quite yellow. It is then evaporated to about one-third of its former bulk, and saturated with 35.35 kilogrammes of soda crystals. A new quantity of chromate of zinc is obtained. The supernatant liquors are still colored yellow, and saved for a purpose which we shall indicate further on.

"The chromate of zinc is washed two or three times in the tubs, by decantation, and with pure water or rain water. The washings are mixed with the previously saved mother liquors. The clear paste of chromate of zinc is drained upon cloth filters, and is there washed two or three times. When it has acquired the proper consistency it is moulded into the shape of troches, which are dried in a stove-room.

"The washings and mother liquors are heated and treated with hydrosulphuric acid, which decomposes the chromates of potassa and zinc held in solution. There is produced a precipitate which is a compound of hydrated oxide of chrome, and of oxide and sulphide of zinc. This compound may be used in painting as a very fast and durable pigment; but its nature and hue may be changed by a calcination and washing.

"This product may be obtained directly in the anhydrous state by evaporating the liquors to dryness, powdering the residuum, mixing it with 18 per cent. of sublimed sulphur, and calcining the mixture until the sulphur is volatilized. The hot substance is then thrown into water, and the anhydrous pigment is collected upon a filter.

"The neutral chromate of potassa and soda may be replaced by the neutral chromate of soda, which is prepared by the calcination of chrome ore with nitrate of soda.*

2. *Chromate of Baryta.*

"Basing ourselves upon the processes which we

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* Mr. R. Wagner has made the analysis of several samples of chromate of zinc, and reports them as follows in his annual of technological chemistry (1861):—

Zinc yellow from England—

Chromic acid	14.94
Oxide of zinc	75.35
Carbonic acid	3.61
Water	6.19
	100.09

The zinc yellows prepared in Germany are generally adulterated with the carbonate or the sulphate of baryta, as is demonstrated by the following analyses:—

	a.	*b.*
Chromic acid	11.88	9.21
Oxide of zinc	45.78	61.47
Sulphate of baryta	42.34	29.32
	100.00	100.00

have indicated for the manufacture of the chromate of zinc, and procuring a chloride of barium free from iron, and the neutral chromate of potassa and soda, we employ the following formula:—

"100 kilogrammes of chloride of barium are precipitated by 82 to 84 kilogrammes of neutral chromate of potassa and soda. The product is washed by decantation, and dried in a stove-room.

"Such is the process by which we have been enabled to produce, in an economical manner, the chromate of baryta which up to the present day had remained a product of the experimental laboratory.

3. *Orange-red Sulphide of Antimony.*

"The preparation of this sulphide, by the processes which we are going to describe, results in a color not yet employed in painting, and which is not altered by dampness, light, or sulphuretted hydrogen. This product and its mode of preparation are new, and are a valuable addition to the new system of painting with zinc pigments.

"One part of natural sulphide of antimony is powdered and dissolved with the aid of heat, in seven parts of hydrochloric acid at 20° Bé., which should be chosen free from lead. The sulphuretted hydrogen disengaged from the first operation is condensed in a milk of lime; that of subsequent operations is employed for preparing the sulphide of antimony as follows:—

"When all the sulphide is dissolved, the solution of acid chloride of antimony is decanted into stoneware vessels which have holes at different heights. The liquor is diluted with pure water until it begins to become turbid, and a white precipitate appears.

The whole is then put into demijohns and submitted to a stream of sulphuretted hydrogen.

"We must not forget to mention that the glass tubes dipping into the antimonial solution should be large, so as not to be obstructed by the red sulphide of antimony, formed by the reaction of the sulphuretted hydrogen with the acid chloride of antimony. The liquor should be stirred often with a wooden stick, and the vases covered or communicating several together, in order not to lose the sulphuretted hydrogen, which may injure the workmen. On that account the last tubes dip into a milk of lime which condenses the excess of gas. The stream of sulphuretted hydrogen is arrested when the saturation is complete, and the precipitate is allowed to settle. The deposit of sulphide of antimony is washed several times by decantation, poured upon filters, and again washed until the water runs without taste. The pigment is then dried in the stove-room at a moderate temperature, which should not be above 40° to 50°, otherwise the sulphide will lose its combined water and turn black.

"This mode of preparing the hydrated sulphide of antimony is a new process of manufacture, since no practical indication of the same is to be found in works on chemistry.

4. *Mixed or Compound Colors.*

"We give this name to pigments of different tones and hues obtained by the combination or mixture of the colors here described with other usual colors, excepting those with a lead or a copper basis.

"We understand that with the chromate and the oxide of zinc, with the chromate of baryta and the red sulphide of antimony, mixed or combined with other usual colors, it is possible to obtain a great many varieties of tones and hues which will not be acted upon by sulphuretted hydrogen. We cannot here give a complete nomenclature; we shall, however, mention the following yellows: Roman yellow, bright yellow, antimony yellow, Mars yellow, Indian yellow, Naples yellow, mineral yellow, and several chrome yellows.

"All of these colors may be obtained by the combination of our new products, and in certain cases with the aid of raw Sienna.

"The greens known under the names of dark English green, light English green, Milori green, green earth, and verdigris, are prepared in the same manner as the yellows, and with the addition of a greater or less proportion of blue.

"The colors are mixed either in the pasty state and before being dried, or after they have been ground.

"We see that the principle of these compound colors consists in the mixture of zinc white with the new colors we have just described, or with other usual colors which are not altered by sulphuretted hydrogen. We also arrive at tones and hues which formerly could not be obtained without the use of pigments with bases of lead and copper, so easily acted upon by certain destructive agents.

"In a preceding description of the yellow chromate of zinc, we said that it was obtained by the reaction of a neutral chromate of potassa and soda upon a pure and neutral sulphate of zinc. The following are new processes for the manufacture of a basic chromate of zinc.

"About 50 kilogrammes of pure oxide of zinc are thrown into a solution of 100 kilogrammes of bichromate of potassa in 400 kilogrammes of hot water. After boiling, the liquor is left to cool off, and, after decantation, the precipitate is washed and dried.

5. *Lemon Yellow.*

"The above decanted liquors and washings are evaporated to two-thirds of their bulk, and receive a solution of sulphate or of any other soluble salt of zinc, in proportion variable with the tone desired. The precipitate, after decanting, is washed, etc.

6. *Pale Yellow.*

"In order to utilize all the raw materials, the liquors from the above operation are saved and boiled with a sulphate of zinc, prepared with 15 kilogrammes of zinc oxide and 7 kilogrammes of commercial sulphuric acid. The precipitate is treated as usual.

"We have also said that compound greens were prepared by the action of sulphuretted hydrogen or sulphur upon the chromate of zinc remaining soluble in the mother liquors and washings; and that various tones and hues were obtained by adding to the chromate of zinc a greater or a less proportion of blue.

"We also state that these greens may be obtained from a solution of chloride of zinc to which is added a suitable quantity of blue liquid or paste, or the materials forming Prussian blue. In this manner the green is directly obtained."

§ 12. *Basic chromate of tin, mineral lake.*

Mineral lake, which is a combination of chromic acid with the oxide of tin, possesses a fine lilac color, and is sought for as a substitute for vegetable lakes in the fabrication of paper hangings and for oil painting.

This lake is prepared by dissolving the neutral chromate of potassa in five or six times its weight of water, and pouring into it a solution of bichloride of tin as long as a precipitate is formed, which is afterwards washed and collected upon a filter. When the chromate of tin is well drained, but still wet, it is ground with half of its volume of nitrate of potassa, and the whole is allowed to dry. The mass is then finely pulverized and thrown by small quantities at a time into a crucible brought to a low red heat, and which holds already some nitrate of potassa. When the decomposition is complete, the crucible is removed from the fire, and left to stand a little while. The supernatant liquid nitrate of potassa is decanted, and the basic chromate of tin is separated from the crucible by means of hot water. It is afterwards washed until the liquors have no alkaline reaction.

The chromate thus obtained is of a dull and pale yellow color, and in order to give it the desired lilac hue it is strongly calcined for one or two hours in a luted crucible, placed in an air furnace and covered with coke. After this calcination the substance is dense, and contains some bright spots. It is easily powdered, and is not acted upon by air, dampness, light, or sulphuric acid.

Mr. Malaguti, to whom the discovery of this lake is due, prepared it by calcining at a dull-red heat and in a clay crucible, an intimate mixture of 100 parts of stannic acid (binoxide of tin) and 2 parts of oxide of chromium. After cooling, the vitrified mass was powdered, and was of a lilac hue, but somewhat grayish, as some people said.

§ 13. *Naples yellow.*

Many believe that this yellow, which is a peculiar combination of oxide of lead and antimonic acid, is extracted from the lava of Mount Vesuvius. Fougeroux de Bondaroy claims that Naples yellow is a composition known at Naples under the name of *giallolini*, the secret of which is held by one individual. He adds, that, having been unable to discover the secret during his travels in Italy, his chemical researches proved to him that this yellow was prepared with white lead, alum, and diaphoretic antimony (antimoniate of potassa). In regard to Naples yellow, Thénard says: "The preparation of this yellow is well known only to those who make it for the arts. It is said to be obtained by calcining, at the proper temperature, a mixture of pure litharge, hydrochlorate of ammonia (sal ammoniac), diaphoretic antimony (a combination of peroxide of antimony and potassa), and alum."

Naples yellow is obtained by processes differing one from another, and which very likely furnish different tones of color.

Fougeroux de Bondaroy has indicated the following recipe:—

White lead	24 parts.
Diaphoretic antimony (antimoniate of potassa)	4 parts.
Sal ammoniac	1 part.
Alum	1 part.

All of these substances should be finely powdered and throughly mixed before they are placed in a crucible which is kept at a red heat for three hours. After cooling, the crucible is broken, and the mass which is very dense and compact, and of a fine yellow color, is finely ground, and then washed several times for the purpose of separating the soluble substances. Lastly, the powder is dried.

Naples yellow is also obtained by smelting, at a low temperature, 3 parts of massicot and 1 part of oxide of antimony.

Two parts of red lead may also be fused with 3 parts of powdered metallic antimony and 1 part of calamine.

Another recipe consists in smelting 5 to 6 parts of lead, 2 to 4 parts of antimony, and 1 part of cream tartar (bitartrate of potassa).

Again it is said that 16 parts of lead, 16 of antimony, 2 of cream tartar, and 1 of common salt, produce a Naples yellow.

Five parts of litharge, two of antimoniate of potassa, and one of sal ammoniac, give a fine yellow.

Lastly, Mr. Guimet, of Lyons, asserts that a handsome yellow may be produced with two parts of red lead and one part of antimoniate of potassa.

A German chemist, Mr. Brunner, has made a special study of Naples yellow, and, after a great many experiments, finds that the finest article is prepared in the following manner:—

One part of tartrate of potassa and antimony or tartar emetic, purified by several crystallizations, is intimately mixed with two parts of nitrate of lead free from copper or iron, and four parts of common salt. The homogeneous mixture is slowly brought to a state of fusion in a Hessian crucible. After cooling, the mass is detached by striking the overturned crucible, and then ground and washed, in order to remove the salt which formed the upper layer of the melted mass.

The yellow is very fine with a properly conducted fire, but too much heat impairs it. The color may be brightened by washings with hydrochloric acid.

Mr. A. Hick, in the *Technologiste*, vol. xxi. page 72, has indicated a mode of preparing a yellow color which resembles Naples yellow.

It is known, says he, that in refining lead the metal is melted in a reverberatory furnace, and presents a large surface to the action of the air. The antimony and other metals usually accompanying lead are oxidized, and their oxides form a sort of scoria on top of the fused lead. These oxides are principally those of lead, antimony, and arsenic; and in order to transform them into a pigment, they are finely ground, and calcined in a reverberatory furnace, or in any other furnace where they are simultaneously acted upon by air and heat. The calcination is begun at a low temperature, which is slowly raised to a red heat. The length of the operation depends on the quantity of material operated upon, and in practice, from one to three days are necessary to calcine 1500 kilogrammes of pulverized oxides.

It is advantageous to mix with the powder, during the latter period of the calcination, a certain quantity of common salt (chloride of sodium). An accurate proportion of salt is not very important, but practice indicates about one-half of the weight of the oxides.

The calcined product is sometimes saturated with sulphuric, hydrochloric, or acetic acid, or exposed to the vapors of acetic acid in tan beds, like those used for white lead. This treatment with common salt and acids improves the quality of the color.

When the color remains constant in the furnace, the oxides are removed, washed, ground, etc.*

The color of Naples yellow varies in tone with the different processes of manufacture, but generally it possesses brightness, depth, and durability. This pigment unites readily with other colors, and enhances the brightness of the yellow ochre with which it is sometimes mixed. Its preparation requires peculiar precautions; for instance, it should be ground upon a slab of porphyry or marble, and collected with an ivory blade, because steel turns it green. It is used on chamois grounds, for fine yellows imitating gold, and for carriages.

§ 14. *Cadmium yellow.*

This salt is of a remarkably fine orange-yellow color, which remains unchanged by fire. It fuses at a white heat, and by cooling, it crystallizes into translucent and micaceous laminæ possessing a magnificent lemon-yellow color. On account of its beauty and durability, this pigment is used in artistic paintings, but its price is still very high.

Cadmium yellow is obtained by passing a stream of sulphuretted hydrogen through a solution of nitrate or sulphate of cadmium. The precipitate of sulphide of cadmium is washed, collected upon a filter, and dried in a stove-room. Thus prepared,

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* The above described process is evidently an economical method for obtaining a color nearly identical with Naples yellow, that is, an antimoniate of lead, the degree of saturation of which is little known. It is possible that the small proportion of arsenic contained in the oxides, modifies the tone of the color, and causes a certain difference between it and real Naples yellow; but then the pigment is poisonous, and should be used very carefully.

the yellow is in the state of impalpable powder which covers very well.

This color may also be prepared in the dry way, by heating in a crucible oxide of cadmium with an excess of sublimed sulphur. The yellow prepared in this manner is not so handsome as the previous one, and does not cover so well.

Blue pigments and cadmium yellow produce very rich and durable greens, which should not be mixed with white lead or other lead compounds, because the latter are decomposed and blackened by the sulphur of the cadmium.

§ 15. *Yellow of antimony and zinc.*

Messrs. G. Hallett and J. Stenhouse, in 1861, took out a patent in England, for the manufacture of colors with an antimonial basis. The following is their mode of operation :—

They take the native oxide of antimony, or the mixed oxide and sulphide, often associated with the gray sulphide of antimony. It is a combination in variable proportions of antimony and oxygen, with more or less sulphide of antimony, oxide of iron, silica, water, and sometimes arsenic, and the color of which varies from a light yellow to a yellowish-red. The gangue is removed as far as practicable, by picking and washing, and the ore is finely ground and sifted. The powder is introduced into large crucibles, muffles, or reverberatory furnaces, where it is carefully calcined at a dull red heat and with the access of the air. The mass is constantly stirred in order to prevent too great an elevation of its temperature. During the operation the powder emits steam, sulphur, and sulphurous acid, fumes of antimony and arsenic, and becomes less fusible. The calcination lasts generally from two to three hours, and is completed when vapors and fumes are no longer disengaged, and when all the antimony has been transformed into anhydrous antimonious acid.

The impure antimonious acid thus produced, is reduced to an impalpable powder by grinding and levigation. After drying, it forms with oil, varnish, etc., a new pigment for painting, which may be combined with other oxides or salts, such as zinc oxide, white lead, chromate of lead.

A yellow color is produced with eight parts of native oxide of antimony, or of oxide mixed with sulphide, or the impure antimonious acid obtained by the above process, three parts of red lead or litharge, and one part of oxide of zinc. The whole is finely powdered and thoroughly mixed, and calcined in crucibles, muffles, or furnaces, until the combination is effected and the yellow color has appeared. The mass is then finely powdered, and ground in oil or in varnish.

The above proportions give good results, but they may be made to vary. Sometimes the proportion of oxide of lead is increased; at other times, the oxide of zinc is suppressed. About four parts of common salt may be employed, in which case the product is afterwards carefully washed. By varying the proportions of the constituent parts, as seen in the examples below, various tones and hues of Naples yellow will be produced:—

	I.	II.	III.
Antimonious acid . .	4 parts	1	3
Oxide of lead . . .	2	2	3
Oxide of zinc . . .	1	1	1

	IV.	V.	VI.
Antimonious acid . . .	1 part	1	2
Oxide of lead . . .	1	1	1
Oxide of zinc . . .	1		

§ 16. *Turner yellow. Kassler yellow. Cassel yellow. Montpellier yellow. Verona yellow. Mineral yellow.*

These various names belong to quite a number of colors, the composition of which is not perfectly established. Nevertheless they appear to result from the combination of a protochloride of lead with variable proportions of oxide of lead.

According to Hahneman, the mineral yellow of Turner is prepared by mixing together twenty-one parts of red lead, and two parts of sal ammoniac (hydrochlorate of ammonia). After fusion in a crucible, the mass is poured upon a marble slab, and then pulverized.

Other persons prepare this color by fusing litharge or white lead with common salt or sal ammoniac. The following is the method practised at Montpellier by Chaptel, and described by him:—

Four parts of finely pulverized litharge are put into a stoneware vessel, and mixed with a portion of a solution of one part of common salt in four parts of water. The stirring is effected with a spatula of glass, lead, or wood, but iron is discarded. The substance swells and becomes hard; it is then broken and mixed with another portion of the saline solution. The stirring is continued with fresh additions of the solution. When the latter is exhausted, pure water is used as long as the substances continue to swell. At last they sink down. The stirring is continued, and when the mass has become perfectly white, smooth, and fine, it is thoroughly washed in water. The paste is then pressed in a cloth, and afterwards distributed in shallow stoneware vessels which are exposed to a moderate but protracted heat. The dome of a porcelain furnace is well adapted to this last operation. The cooling is slow, and the result is a chamois yellow of a pure hue, but not so bright as Naples yellow.

Mineral yellow is produced by a mixture of English litharge and sal ammoniac; its color is a bright lemon-yellow without durability. It is prepared with two or three parts of English litharge (yellow protoxide slightly vitrified), and one part of sal ammoniac, ground together in a marble mortar with a little water. The resulting paste is put into an unglazed clay dish, which is heated in a reverberatory furnace, slowly at first to evaporate the water. The heat is then increased by degrees until the ammonia has entirely escaped. The dish is removed from the furnace, and the color is of a bright lemon-yellow. It is employed mostly for coach painting and theatrical scenery.

Mr. Mérimée says that a more durable mineral yellow is prepared by grinding separately and mixing afterwards:—

Metallic bismuth	3	parts.
Sulphide of antimony	24	"
Nitrate of potassa	64	"

The mixture is introduced by degrees into a heated crucible. After fusion, the substances are thrown into water and stirred as long as it is necessary. The precipitate is washed by decantation until the water is tasteless, whence it is collected upon a filter and well dried. The resulting oxide is in the shape of a fine powder colored a dirty yellow. One-eighth of one part of this dry oxide is mixed with one part of hydrochlorate of ammonia, and sixteen parts of pure litharge, and the whole is fused in the manner previously indicated. Should a given tone of color be desired, it is necessary that the degree of temperature and the length of operation should always be exactly the same.

There are other processes for preparing this color. For instance, there are manufacturers who produce it by maintaining for some time and exposed to the access of the air, a neutral chloride of lead in fusion. This salt is partly decomposed; chlorine is disengaged, and the reduced metal combines with the undecomposed chloride of lead.

Others prefer melting together one part of chloride of lead and four parts of red lead.

Lastly, some persons heat ten parts of massicot and one part of sal ammoniac. The molten mass is divided into two layers, the lower one being metallic lead, and the upper one, a pure and bright mineral yellow.

This color is somewhat difficult of preparation, and great cleanliness is necessary. Many tones and hues are to be found in the trade depending on the proportion of basic chloride. But in every case, it may be deepened by a second fusion, or lightened by a fusion with a small proportion of sal ammoniac.

It is employed especially for coach and theatrical painting, and the color is deepened by an addition of chrome yellow. It should not be placed in contact with sulphur compounds.

The Mérimée yellow is very rich of tone, and very durable. It is sought for artistic painting, and is sold in the trade under the names of *antimony yellow* and *superfine mineral yellow.*

§ 17. *Mineral straw-yellow.*

This very bright color may be considered as a basic sulphate of lead (a combination of sulphuric acid with an excess of oxide of lead). It is obtained by melting in a crucible a mixture of equal parts of sulphate of lead and litharge. After fusion, the mixture is poured out upon a slab, and when cold it is powdered.

The pure mineral straw-yellow possesses a finely toned yellow color, is durable, and covers well. But it should not be exposed to sulphuretted gases. That found in the trade is very variable in tone, on account of the large proportion of lead introduced into it.

§ 18. *Mineral turbith.*

The names of mineral yellow and *mineral turbith* are given to a subsulphate of mercury, which is prepared as follows:—

One part of mercury is boiled with two parts, at least, of sulphuric acid at 66° Bé., in a stoneware retort heated in a covered furnace. There is an abundant production of sulphurous acid, and, when the reaction is completed, the retort is broken, and the acid sulphate of mercury is dissolved in boiling water. The mass becomes decomposed, and, after repeated washings with hot water, acquires a pretty lemon-yellow color. Lastly, it is collected upon a filter and dried. Mineral turbith is not much used, and it is said to become decomposed in the air. This yellow, with Prussian blue, produces a magnificent green, finer than that prepared with orpiment, and without a tendency to become black. It is highly poisonous.

§ 19. *Orpin or orpiment. Yellow sulphide of arsenic. Yellow realgar.*

This mineral, which is a trisulphide of arsenic, has a fine gold-yellow color, and is in the shape of a mass of soft and flexible laminæ, semi-translucent, and easily separated, also in oblique prisms. It is tasteless, odorless, and presents a lamellar fracture. More fusible than arsenic, it burns with a blue flame and produces a garlic smell. This mineral is composed of—

Arsenic	63.98
Sulphur	36.02
	100.00

It cannot be combined with pigments holding lead or certain other metallic compounds, because it blackens them.

Orpiment is found in the natural state often mixed with realgar or bisulphide of arsenic in secondary formations, but not in sufficient quantity for the arts. It is found in Hungary, Styria, Suabia, Bohemia, Walachia, the East, Peru, etc.

Artificial orpiment, or yellow sulphide of arsenic, has properties somewhat different from those of the natural article. It appears to be a mixture of 96 parts of arsenious acid and 6 parts of sulphide of arsenic. The following is its mode of fabrication:—

1 part sublimed sulphur, finely powdered, and passed through a silken sieve, is thoroughly mixed with 2 parts of powdered arsenious acid. The mixture is introduced into a crucible which is covered with another crucible, or, better still, with a condenser for collecting the sublimate. The latter is an opaque

mass, the color of which varies from a clear yellow to a red, according to the manner in which the fire has been conducted, or the greater or less thoroughness in the mixing of the sulphur and arsenic. By varying the proportions of sulphur, and conducting the operation with more or less rapidity, all the intermediary tones and hues between the extreme colors may be obtained.

Orpiment is an extremely poisonous color, which requires great precautions in its preparation and handling. Moreover it is not durable. It is employed especially in oil painting, and produces with Prussian blue a handsome green, which is, however, liable to turn black.

The name of *royal yellow* is sometimes given to a sulphide of arsenic obtained by precipitation in the wet way.

Mr. R. Wagner says that an extremely fine yellow orpiment is prepared with sulphide of arsenic and sulphate of baryta, and might replace chrome yellow if there were no arsenic in it. This pigment is prepared as follows:—

2 parts of finely-ground sulphate of baryta are calcined with 1 part of powdered charcoal, tar, or oil waste, etc. The calcined mass is pulverized again, mixed with 1 part of ground orpiment, and boiled in water. After filtration the liquor contains a sulpho-arsenite of baryta, which may be precipitated by diluted sulphuric acid. Chloride of barium may be added before the addition of the acid, and in this manner the precipitated pigment is lightened in color.

The disagreeable and unhealthy escape of sulphuretted hydrogen may be avoided by adding to the solution of chloride of barium a quantity of arseniate of potassa in hydrochloric acid, proportional to the amount of sulphuretted hydrogen produced.

§ 20. *Arsenite of lead.*

Arsenite of lead is also a highly poisonous pigment, which is often substituted for orpiment. Its yellow color is equally fine with it, more durable, and with a good body.

The arsenite of lead is obtained from an intimate and finely powdered mixture of 10 parts of arsenious acid and 7 parts of litharge, which is brought to a red heat in a crucible placed in a furnace having a good draft. When the substances are in a quiet state of fusion, they are poured upon a marble and afterwards finely ground.

By varying the proportion of lead, *i. e.*, by increasing that of litharge, the arsenites become redder, especially if the heat be more protracted.

§ 21. *Massicot. Litharge.*

Massicot is a pulverulent yellow protoxide of lead, which when fused is called litharge.

If metallic lead be placed upon the hollow hearth of a reverberatory furnace having a fireplace on two opposite sides, it soon melts and becomes oxidized on the surface. By removing the oxidized portions a new quantity of oxide is formed, and so on until all the metal is transformed into a fine yellow protoxide, or massicot. It is sometimes employed in painting, and it is more or less reddish according as the heat has been more or less raised, or the lead is purer, etc.

Litharge is a protoxide of lead which has been melted. Its yellow color often acquires a reddish hue, which is due either to impurities, or to the temperature, or to its more or less sudden cooling.

It is seldom that the manufacturer of pigments is obliged to prepare his litharge, which can be had in the trade at moderate prices, and which results from the cupellation of lead in metallurgic works.

§ 22. *Iodide of lead.*

This yellow, which possesses the brightness of orpin and of chromate of lead, is prepared by precipitating a solution of nitrate or acetate of lead with a solution of iodide of potassium. The nitrate of lead produces a brighter article than the acetate. Iodide of lead is soluble in 1235 parts of cold, and 192 parts of boiling water. The latter by cooling deposits spangles of iodide.

We are indebted to Mr. Huraut for a more practical and economical method for the manufacture of iodide of lead than that generally practised. The following is a description of the process:—

Take of—

Iodine	100 parts.
Iron filings	15 "
Quicklime	25 "
Water	sufficient,

and make with these substances a paste which is gently heated and continually stirred. When the combination is effected, that is, when all the iodine has disappeared, more water is added. After settling and decanting, the residuum is treated with a fresh portion of water and the mixed liquors are filtered. They hold iodide of calcium, which is decomposed by a solution of 152 parts of neutral acetate of lead, or of 132 parts of nitrate of lead. The precipitate is washed two or three times only, and then dried at a moderate temperature.

The above proportions give 175 parts of a micaceous iodide of lead, which is of a magnificant orange-yellow color.

This pigment is very bright, but is affected by the sun and sulphurous emanations. It is also poisonous.

§ 23. *Uranium yellow.*

Uranium yellow is extracted from the uranium-pech-blende or pech-urane, which was formerly discarded, but which at the present time is mined with profit in Germany, especially for furnishing glass-makers with a pigment which colors glass a very handsome greenish-yellow.

Mr. Patera was the first who proposed a manufacturing process, which may be summed up as follows: Powdered pech-urane is mixed with chalk, and by calcination forms a uranate of lime which is treated by sulphuric acid. The solution is boiled with metallic iron, in order to reduce the oxide of uranium to the protoxide state, and is afterwards largely diluted with water. A basic sulphate of protoxide of uranium is precipitated, and is separated from the basic sulphate of protoxide of iron by being dissolved in the smallest possible quantity of sulphuric acid. An addition of water precipitates it again. The pure basic sulphate of protoxide of uranium, thus obtained, is used for the preparation of other combinations of uranium.

Mr. Patera has since modified this process. The pech-urane is calcined with lime in a reverberatory furnace, then treated by sulphuric acid mixed with a small proportion of nitric acid, which dissolves the oxide of uranium. To this impure solution an excess of carbonate of soda is added, which forms a soluble carbonate of soda and of oxide of uranium. Sulphuric acid separates from it an uranate of soda, which is sold under the name of uranium yellow.

This process is said by Mr. C. F. Anthon, to furnish a product which is not very well received in the trade.

Mr. Anthon having had to work several tons of pech-urane, with a variable yield of 10 to 70 per cent. of uranic oxide, it is interesting to chemists to know his process, which presents several advantageous features.

The ore is pulverized as finely as possible, which is difficult with the poor qualities. A clear and liquid paste is made with the powder and water, which is treated with a mixture of equal parts of nitric and hydrochloric acids. These need not be pure, and may contain a certain proportion of sulphuric acid. The operation should take place in the open air or under a chimney with a good draft, and the vessels used are of varnished stoneware of a capacity of 20 litres for 12 or 13 kilogrammes of powdered pech-urane, or of cast-iron holding from 50 to 100 kilogrammes of ore. The materials are constantly stirred, as long as there are red vapors disengaged, especially after each addition of acids.

By a previous calcination of the ore, the escaping acid fumes will be less abundant, and there will be a sensible saving of nitric acid, since aqua regia may then be composed of three parts of hydrochloric acid to one part of nitric acid. The action of the aqua regia is very energetic, even without the aid of heat, and especially when the ore is not calcined; the produced heat is then so great that the ore is entirely subdivided and corroded.

The proportion of nitric acid cannot be even approximately determined; it depends entirely on the very variable quality of pech-blende used, and whether the ore is in the raw state or calcined. At all events, the end of the decomposition is ascertained by the absence of effervescence and of red vapor.

As soon as a small addition of nitric acid fails to produce a sensible reaction, the paste, which should have been kept at about the same degree of consistency by the addition of water if necessary, is then evaporated and stirred until it appears dry. When this point is reached, the kettle is brought to about a red heat, without reaching it, however.

The dried mass is lixiviated with water, and the mixed liquors, which mark from 8° to 12° Bé., are treated with carbonate of soda, in slight excess, that is, until the latter substance can be recognized by the taste. A great excess is to be avoided.

The liquor thus obtained is not clear, and is colored a yellowish-brown by the precipitated oxides. It is made to boil in a cast-iron kettle, which is afterwards allowed to cool very slowly until the next morning, by closing the flues and covering the vessel.

The next day, the clear and yellow liquor above the deposit is siphoned off. It is a nearly pure solution of urano-sodic carbonate. The thick deposit is drained in cloth sacks (0.80 metre long, and 0.20 to 0.22 metre wide), fixed to a wooden frame, and which are compressed when the liquors have ceased to run naturally. The pressed cake is boiled again with water, and a small proportion of soda, in order to extract what may remain in it of uranium oxide. All the uranic solutions are then concentrated into a cast-iron kettle, and the urano-sodic carbonate which separates is "fished," that is, collected in glazed dishes suspended in the boiling liquor. When the deposits no longer take place, the mother liquors, which still hold a notable proportion of oxide of uranium, are mixed with the washings of the dried mass, after the treatment by the acids.

The collected urano-sodic carbonate forms a crystalline greasy powder, which is but slightly soluble in water, and is of a bright lemon-yellow when pure. But as this carbonate is not always of constant composition, or in favor with the trade, it should be changed by a further treatment, into ammoniacal uranium oxide, of a much deeper yellow, and which is more eagerly sought for, on account of the greater proportion of uranium oxide it yields.

The urano-sodic carbonate is *slowly* dissolved in water, and the solution is sufficiently saturated when it marks from 15° to 18° Bé. The impurities are separated, either by filtration, or by allowing the liquors to stand.

Although neither of these operations is difficult, it is preferable in practice to put the raw urano-sodic carbonate into small wooden tubs (5 to 6 centimetres high, and from 20 to 25 centimetres in diameter), through which water is made to pass until all the carbonate is dissolved. By this treatment, the foreign substances remain insoluble.

The pure solution of urano-sodic carbonate is poured into a cast-iron kettle, and is decomposed by solutions of sulphate or hydrochlorate of ammonia (according to the market value of these salts), which are added at intervals and in quantities to be determined by experience. The operation is completed when effervescence ceases, or when carbonate of ammonia is disengaged. The yellow ammoniacal oxide is collected (fished) in dishes, as in the preparation of the urano-sodic carbonate, and is washed and dried.

When the boiling mother liquors, after the addition of a small quantity of ammoniacal salt, do not give a precipitate, or are without alkaline reaction, they are removed from the fire and preserved for another operation with the washings, since they yet hold a certain proportion of oxide of uranium.

The proportion of ammoniacal salts employed is small, because enough, and no more, is added for the acid of the salt to saturate the soda of the carbonate. As the anhydrous urano-sodic carbonate contains 22.9 per cent. of soda, 100 parts of it require 49 parts of hydrochlorate of ammonia (sal ammoniac).

Moreover, if we consider that the sulphate of ammonia may be had for about one-fourth of the price of carbonate of ammonia, and that in other methods of preparing the oxide of uranium the weight of carbonate of ammonia employed is from three to five times that of the sulphate required by the author's process, the superiority of the latter method is evident, besides possessing other advantages.

While engaged in the manufacture of uranium oxide by the method thus described, the author made the following analysis to arrive at the composition of the urano-sodic carbonate which he could not find anywhere.

a. 30 grains of the compound gave 7.1 grains of carbonic acid, that is, 23.7 per cent.

b. 30 grains were treated by a solution of sal ammoniac, evaporated to dryness, and then gently calcined to expel the excess of ammoniacal salt. The same treatment was repeated with a small addition of ammonia, and, after washing and heating, the residue was 15.8 grains of oxide of uranium, that is, 52.7 per cent.

c. The liquors and washings of the previous test, being evaporated to dryness and gently calcined, left a residue of 12.9 grains of chloride of sodium, corresponding to 6.7 grains of soda, or 22.9 per cent.

Therefore, the urano-sodic carbonate, precipitated in the shape of a slightly soluble and lemon-yellow colored powder, during the evaporation of the aqueous solutions of this carbonate, has the following composition:—

Oxide of uranium	52.7
Soda	22.9
Carbonic acid	23.7
Water	0.7
	100.0

and its formula is $2(NaO.CO^2) + U^2O^3.CO^2$, which composition corresponds with that of the urano-potassic carbonate analyzed by Ebelmen.

This compound is slowly dissolved in water, and the saturated solution, at the temperature of about 15° C., has a specific gravity of 1.161.

The urano-sodic carbonate loses a little water when heated at a low temperature. By increasing the temperature, and even below a red heat, it loses the greater part of its carbonic acid, and acquires a light brick-red color. It will lose more carbonic acid at a red heat, but even by maintaining it at that temperature for half an hour it cannot be entirely deprived of acid.

§ 24. *Gamboge.*

Gamboge is a resin which oozes from the broken branches, or from incisions made in the trunks of various trees which grow in Siam, Ceylon, and Cambodia. This substance is exported in the shape of cylinders or cakes, which are yellowish-brown at the exterior and orange-red inside, very hard, brittle, and with a bright fracture. The powder is of a deep-yellow color. This resin is colorless, slightly poisonous, and very purgative. Insoluble in water, but soluble in ether and alcohol, it is composed of 80 per cent. of pure resin and 20 per cent. of gum. According to Mr. Lefort, the yellow resin may be separated from the gum by solution in purified essence of turpentine. The greater part of the essence may be recovered by distillation, and the residue, being evaporated to the consistency of an extract at a low temperature, abandons a hyacinth red resin in lump, which is of a bright-yellow when powdered. It mixes very well with oils.

Gamboge is employed especially in water and miniature painting. The article purified in the above-mentioned manner possesses more body than the raw material, but the price is too high for extended application.

§ 25. *Jaune Indien* (*Indian yellow*). *Purree.*

We now find in the market a coloring substance, which is known in England under the name of *purree*, and in France, under that of *Jaune Indien* (Indian yellow). The raw substance is in the shape of rounded lumps, weighing from 150 to 200 grammes, brown-green at the exterior, and of a very rich orange-yellow inside. It emits a smell similar to that of *castoreum*, is slightly soluble in cold water, but insoluble in alcohol and ether. When pure, it burns like tinder, and leaves a very small residuum. It may be purified by washing its powder with boiling water, and drying at a low temperature. Purree is a handsome yellow pigment, non-poisonous, and durable, but which dries slowly.

Indian yellow is still sold at a high price, and is generally adulterated with chrome yellow or other yellow substances. Mr. Stenhouse, from an analysis made of Indian yellow, ascertained that it was a combination of magnesia with a peculiar organic acid. This result gave to Mr. R. Wagner the idea of preparing it artificially, and the following notice was published in the *Technologiste*, vol. xxi. page 122:—

"There is brought from the East Indies and from China, under the name of *purree*, a yellow substance which, from the researches of MM. Erdmann and Stenhouse, consists principally of a combination of magnesia with an organic acid, to which the name of *euxanthic acid* has been given. Pure purree or Indian yellow is a handsome yellow color, which is often preferred in oil painting to either the chromate of lead or of zinc, to the royal yellow (precipitated sulphide of arsenic), and even to the sulphide of cadmium. The Indian yellow, prepared in Paris, does not appear to be obtained by purifying the raw material in boiling water, but by using the pure euxanthic acid. I have also ascertained by the analysis of a Parisian sample, that the inorganic basis is not magnesia alone, but magnesia and alumina. A sample, dried at 100° C. and calcined, gave the following results:—

Organic substances and water	52.3
Inorganic residuum	47.7
	100.0

"I have ascertained that the organic substance is the euxanthic acid, by boiling the yellow color in hydrochloric acid, in which it is entirely soluble. By cooling, pale-yellow needles were deposited, which presented all the reactions of euxanthic acid. Under the action of heat they melted, and produced a crystalline sublimate (euxanthon). The calcined residue was composed of—

Alumina	72
Magnesia	28
	100

"This composition quite entirely agrees with that of spinel ($Al^2O^3.MgO$), and gives a clue for the preparation of euxanthic yellow.

"We know from the researches of Mr. Habich that when one equivalent of a magnesia salt is mixed with an equivalent of an alumina salt, and when sufficient sal ammoniac has been added to partially prevent the precipitation of the magnesia, the precipitate of alumina caused by an addition of ammonia, will carry with it enough magnesia to form an artificial hydrated spinel. I have also found that the aluminous compound, equally with pure magnesia, possesses the property of forming with the coloring substances a lake which is remarkable for its porosity.

"We may, therefore, obtain the euxanthic yellow in the following manner. We make a solution of—

Potassa alum	45	grammes.
Sulphate of magnesia	13	"
Sal ammoniac	6	"
Water	250	"

"We dissolve in another vessel a few grammes of euxanthic acid in diluted ammonia, and mix this solution with the previous one. The mixture is precipitated in the cold by ammonia, without any excess. The yellow and bulky precipitate thus formed is washed, pressed, and dried. This product, however, is not to be compared in fineness with that manufactured in Paris, and the preparation of which is kept secret."

§ 26. *Aurum mussivum. Mock gold. Mosaic gold. Cat's gold. Painter's bronze, etc.*

This compound is a bisulphide of tin, which is composed of—

Sulphur	35.37
Tin	64.63
	100.00

It is employed in oil painting for enhancing the tones or the reflex of bronzes, for gilding wood, etc. It is formed of bright and translucent scales, soft to the touch, odorless and tasteless, and insoluble in water, alcohol, ether, and oils. The following is the more generally employed process for the manufacture of mosaic gold.

12 parts of tin are amalgamated with 6 parts of mercury, and the amalgam is ground with 7 parts of sublimed sulphur, and 6 parts of sal ammoniac. The whole is introduced into a strong glass matrass, which is moderately heated upon a sand-bath until white fumes or sulphuretted hydrogen are no longer produced. The temperature is then brought to a red heat. After cooling, the glass vessel is broken, and the greater part of the mosaic gold is found in the

shape of a scaly mass, covered with other crystalline and bright scales, which result from the sublimation of a part of the compound. The more crystalline portions are separated, and form a superior quality.

There are other recipes in which the proportions of tin, mercury, and sulphur vary. But nothing proves that they are better than the preceding one.

The amalgam of tin furnishes the finest article; but as the mercury is generally lost, a more economical process has been sought for, which produces a cheaper, but not so fine an article.

Out of many formulæ, we select the following ones: Calcine together

Sulphur	1 part
Protoxide of tin . . .	2 parts

Or

Sulphur	3 parts
Protoxide of tin . . .	4 "
Sal ammoniac . . .	2 "

It results from the researches of Mr. Lefort that all the art in the manufacture of aurum mussivum rests on the mode of conducting the fire. Too low a temperature gives a light-yellow product; more heat results in a deep-yellow color; too much heat imparts a grayish hue.

§ 27. *Nankin yellow.*

It is said that a fine nankin yellow color is obtained by drying, and then calcining, a concentrated solution of nitrate of lead, in which has been mixed a small quantity of powdered peat.

§ 28. *Chlorophyl.*

During recent researches on the green coloring matter of leaves, Mr. Fremy has succeeded in separating it into two principles: one, which is blue, is called *phyllocyanin;* and the other, which is yellow, bears the name of *phylloxanthin.* These coloring substances, under the influence of light, produce insoluble combinations, in which it has been possible to vary the affinity of the metallic oxide for the organic matter. The blue principle of chlorophyl is more easily altered than the yellow one, and, under certain circumstances, it may lose and reacquire its color. For separating the two coloring principles which give to chlorophyl its green coloration, 2 parts of ether are shaken with 1 part of slightly diluted hydrochloric acid, in a glass-stoppered bottle. If the substance resulting from the decoloration of chlorophyl be shaken a few seconds with the above liquid, a remarkable reaction is produced: the ether is rendered yellow by the yellow coloring principle which it has retained; the acid reacts upon the decolored portion of the chlorophyl, and reproduces a magnificent blue substance. Under the influence of bases the green color of leaves is transformed into a fine yellow, which is soluble in alcohol. It is this transformed yellow which is employed for the separation of the constituent blue and yellow. This substance will form an insoluble combination with alumina, that is, a yellow lake which will deliver its color to neutral solvents, such as alcohol, ether, and bisulphide of carbon. We believe that the day will come when the arts will utilize the green and yellow lakes, which are so easily prepared with chlorophyl.

SECTION IV.

RED COLORS.

§ 1. *Red ochre.*

When considering the yellow ochres we indicated the mode of manufacture of red ochres, and we added that the oxide of iron which forms their basis acquires the most varied tones and hues under the influence of heat. The sesquioxide of iron obtained by the calcination in a muffle, and with the access of the air, of the sulphate of protoxide of iron, is either orange-red, blood-red, flesh-red, or carmine-red, accordingly as the heat has been more and more increased. A white heat will give it a violet tinge, and artists use this article under the name of *violet from iron.* Some others are reddish-brown, others are grayish. The same principle applies to the manufacture of the red colors employed for painting on porcelain and glass.

Analogous colors have been used for a long time in oil painting, and MM. Bourgeois and Colomb-Bourgeois, Ferrand-Dosnon, and others, have successfully manufactured certain reds, called Mars reds, browns, and violets, which were carefully prepared from pure copperas.

These changes in the coloration of the oxide of iron are reproduced in the majority of substances which contain it, especially the earths. Moreover, when, besides the iron oxide, there are other oxides, calcination will produce different hues which may be as useful as the reds and browns we have mentioned. Thus, water, which forms with the oxide of iron a hydrated combination of a pale-yellow color, will be replaced by zinc oxide if the two oxides are calcined together, and the resulting compound will have a fast and durable color. Alumina produces an orange aluminate. The oxides of manganese, cobalt, nickel, copper, etc., form with the oxides of iron certain browns possessing a depth of coloration in a ratio with their proportion in the compound.

§ 2. *Colcothar. English red or rouge.*

This is a red sesquioxide of iron, which forms a very durable and bright color, and is obtained by the calcination of the green sulphate of iron (copperas) upon iron plates, until it has lost all its combined water and has become white. It is then pulverized, placed in stoneware pots, and submitted to a red heat. During the operation, sulphurous acid and glacial (Nordhausen) sulphuric acid distil over, and the residue of the retort is a hard mass which is coarsely powdered, washed, dried, finely ground, and sifted. The finer qualities are obtained by levigation (floating). The latter, after drying, are sometimes calcined anew, in order to increase their brightness.

Colcothar is also produced by the wet way, in mixing a solution of sulphate of iron with another of carbonate or, better still, bicarbonate of soda. There is formed a soluble sulphate of soda, and a precipitate of carbonate of protoxide of iron, which is soon transformed into hydrated sesquioxide of iron. This is washed, dried, and calcined at a red heat in clay crucibles.

It is said that, when the precipitation is effected in hot liquors, the colcothar is finer, more velvety, and deeper in color.

It may be mixed with other iron colors, or calcined with lampblack, for obtaining various tones of color.

In the latter case, there is a partial reduction of the red oxide of iron to the black magnetic state.

§ 3. *Armenian bole. Ochreous clay. Lemnos earth. Oriental bole. Red bole.*

These various names apply to a yellowish-red pigment, which was formerly imported from the East, but which is now prepared from certain earths found at Meudon, in Burgundy, near Saumur, Blois, etc., and which contain clay, oxide of iron, silica, lime, and magnesia.

The finest pieces are picked up, and softened in water, then lixiviated for separating the coarse and hard particles. The finer portions are allowed to settle, and the deposited paste is dried in the sun, or moulded into troches or balls. This color is durable, but the red is somewhat yellowish.

§ 4. *Iron minium.*

The iron minium is a red color, prepared in Belgium by Mr. de Cartret. It is a mixture of clay and oxide of iron which is in the shape of a fine powder having a deep red-brown color. Its composition is—

Hygroscopic water	2.75
Oxide of iron	68.27
Clay	27.60
Alumina	0.27
Lime	0.40
	99.29

An iron minium prepared in Holland was found by Mr. Bleekrode to be composed of—

Water	6.00
Oxide of iron	85.57
Clay	8.43
	100.00

The difference between the iron minium and the red ochre consists, therefore, in the proportion of peroxide of iron. In ochres, the proportion of oxide is not over 39 per cent., and generally is much less. Colcothar or English rouge contains sometimes not more than 40 per cent. of oxide, the remainder being sulphate of lime. The *Berlin brown-red* is prepared with the iron residue of the manufacture of alum, and always contains free sulphuric acid.

The iron minium is, according to Mr. Wagner, more economical than that of lead, in the ratio of 20 to 39.

§ 5. *Red-brown.*

Red-brown is quite a handsome reddish substance, very durable, but little used. It is obtained by fusing in a clay crucible, 1 part of red oxide of iron and 10 parts of litharge or red lead, which have been thoroughly mixed. After cooling, the mixture is ground.

§ 6. *Red lead or minium.*

Red lead or minium is a very bright orange-red powder, composed, says Mr. Dumas, of two parts of protoxide, and one part of binoxide of lead. It is prepared by pulverizing massicot (yellow litharge), and submitting it to a red heat in a reverberatory furnace, where a portion of the protoxide passes to the state of binoxide. If the product be heated two or three different times, it bears the names of *two fires* or *three fires red lead*, and is of a very rich red color.

Red lead is also manufactured by decomposing at a high temperature white lead or carbonate of lead. This salt loses its carbonic acid, and leaves a residuum of red lead. We shall now describe the manner in which this pigment is manufactured at Portillon, near Tours.

We have already seen (white colors) that the oxide of lead produced at the works of Portillon is separated into two parts: one for the manufacture of white lead, the other for that of red lead.

The crude oxide is powdered and separated from the still remaining metal (blue lead) in a small mill. This apparatus is composed of a horizontal and circular cast-iron plate upon which rolls a cast-iron mill-stone. Below the plate and between the cast-iron bottom of the tub which incloses the whole, there is the stirring apparatus proper.

The mode of working is as follows: The crude oxide is put into the mill and ground under the stone; the stirring apparatus keeps the light particles in suspension in water, and they are carried with it, through the overflow of the tub, into the various settling tanks below. The heavy unoxidized lead remains at the bottom of the mill tub, and is now and then removed by a trap door, to be oxidized again in the furnaces. The circulation of water between the head and tail of the complete apparatus is kept up by a chain and buckets. There are three such mills at work, one being especially intended for the grinding of the purest oxides for the red lead used by flint glass-works.

When the settling tanks have received a sufficient quantity of oxide the latter is made to flow into a basin near the furnaces, where it loses the greater proportion of its water.

The drained oxide is then placed in rectangular sheet-iron trays, capable of holding 15 kilogrammes of litharge (massicot) each. 100 filled trays make a charge, and are put into the hot furnaces at the end of each day. All the openings are closed, especially that of the chimney, which is shut with a well-fitting damper. The same trays are submitted three or four times to the same treatment, after which the oxide or massicot has become red lead. This substance is in the shape of more or less coarse lumps, the color of which is not the same in all the trays; but the mixing of the whole insures a certain regularity of coloration.

The red lead is then powdered in a ventilator, the blades of which break the pieces. The light portions are carried, by the draft of air, up a sheet-iron pipe 12 metres high, and are collected in a sheet-iron reservoir. This mode of powdering is interesting, and its employment should be more extended. The red lead is prevented from falling upon the blades of the ventilator, except in small quantities at a time, by means of a distributing apparatus composed of a grooved cast-iron cylinder, which turns slowly. The grooves receive the red lead. The salubrity of the apparatus is still further increased by a special fan, which exhausts the air on top of the box into which the red lead to be ground is poured. The workman is therefore in the middle of a draught which carries all of the dust from him. The air, exhausted by the fan, passes through long wooden boxes, where it leaves the greater part of the dust, and is then carried out into the atmosphere by means of a high stack.

§ 7. *Orange mineral.*

Orange mineral, according to Mulder, is a definite combination of protoxide and binoxide of lead, in which there remains a small proportion of undecomposed white lead. This chemist believes that the following analysis gives the correct composition of orange mineral:—

Protoxide of lead	73
Binoxide of lead	25
Carbonic acid	2
	100

The greater the proportion of binoxide of lead, the deeper is the red hue of orange mineral.

The following is the mode pursued in the manufacture of this pigment at the works of Portillon, near Tours.

We know that orange mineral results from the calcination of white lead. This substance is coarsely broken and put into sheet-iron trays similar to those employed for red lead, and with which the oxidizing furnaces, hot from the day's work, are charged. When the action of the heat is completed, the orange mineral is removed from the fire, cooled, and then thrown into the distributing apparatus of a grinding ventilator, which is similar to that used for red lead. The powdered orange mineral falls upon a horizontal metallic sieve, and the draft created by a special fan prevents any dust from flying about the rooms.

§ 8. *Realgar, or ruby of arsenic.*

Realgar is a yellow-red bisulphide of arsenic, which is found native in certain of the old rocks, but which is more generally prepared by melting in a crucible a mixture of 8 parts of arsenious acid and 4 parts of sublimed sulphur. The hard, brittle, and opaque substance remaining in the crucible after cooling, is powdered. This poisonous pigment is not very durable, and should not be mixed with lead or mercury colors, which are decomposed by it.

§ 9. *Cinnabar and vermilion.*

We find in the natural state, and we manufacture artificially, a fine blood-red color, which is called *cinnabar*, when crystalline, and *vermilion*, when powdered. This red sulphide of mercury is found in all mercury mines.

1. *Manufacture by the Dry Way.*

Cinnabar is prepared at the mercury mines of Idria, by grinding finely in revolving tuns, 85 parts of mercury and 15 of sulphur. The mixture is then heated in cast-iron cylinders, and sublimed in condensers made of clay. The vermilion is obtained by grinding the cinnabar in water.

Mr. Ritter assures us that the renowned Holland vermilion is prepared by grinding thoroughly a mixture of 1 part of sulphur and 2 of mercury, and by adding to 100 parts of the mixture 2.5 parts of granulated lead or red lead. Each sublimation pot receives about 100 kilogrammes of mixture, which is heated as shall be explained further on. After eighteen or twenty hours of cooling, the pots are broken, and their contents ground in a mill. The lead, in the state of sulphide, remains at the bottom of the vessels.

Mr. Tuckert has also indicated the following different mode of preparation, which is pursued successfully in Holland:—

An intimate mixture is made of 75 kilogrammes of sublimed sulphur (sifted) and 540 kilogrammes of mercury (passed through a chamois skin). The whole is moderately heated upon a shallow iron pan, and the resulting ethiops (black sulphide) is coarsely broken, then ground and kept in jars. Its transformation into cinnabar is effected in large clay pots, well luted, and brought to a dark-red heat in isolated furnaces. The operation begins with the contents of two or three jars of ethiops. The substance becomes inflamed, and as soon as the flame diminishes in intensity the pots are covered with a well-fitting thick iron plate. The fire is kept up for thirty-six hours, and is so regulated that the flame produced by removing the iron cover will rise to about 10 or 12 centimetres above the opening of the pot. The sublimation is aided by stirring the mass every half hour with an iron rod. New additions of ethiops are made every four or five hours. The cinnabar is deposited upon the inward surfaces of the apparatus. After cooling, the pots are broken, and the pigment is finely ground in a mill. The powder is afterwards levigated in order to arrive at a greater degree of comminution, for the finer the vermilion the greater are its fire and brightness.

It is recommended for this manufacture to operate on a large scale with pure materials, to heat at the proper point, and to volatilize all the sulphur which is not combined.

2. *Manufacture by the Wet Way.*

Vermilion may also be obtained by the wet way in a state of impalpable powder. This is the method employed by the Chinese in preparing, by scarcely known processes, the so-called Chinese vermilion, which is one of the finest and the most sought for in the trade. All the processes proposed in Europe up to the present time are based upon the employment of a caustic alkali, generally potassa. We shall rapidly describe four processes: one by Mr. Kirchoff, of St.

Petersburg; another by Mr. Brunner, of Berne; the third by Mr. Jacquelin, of Paris; and the fourth by Mr. Firmenich, of Cologne.

A. *Kirchoff Process.*

This process is somewhat difficult of operation. 300 parts of mercury are ground in a mortar with 68 parts of sublimed sulphur, which has been moistened with a few drops of caustic potassa. The ethiops, or black sulphide of mercury thus formed, is mixed with 160 parts of caustic potassa dissolved in a very small volume of water. The whole is heated upon a sand-bath for a half hour, and water is added to make up for that evaporated. After that time no more water is introduced, and the substance which is kept stirred becomes brown and gelatinous, and then red. When all of the mixture has turned a fine red color, it is carried to the stove-room, and is there now and then stirred. Lastly, the vermilion is washed several times, drained, and dried at a low temperature. Sometimes it is digested in caustic potassa.

B. *Brunner Process.*

Take 300 grammes of mercury, 114 of sulphur, 75 of hydrated potassa, and 450 grammes of water. Thoroughly mix and grind the mercury and sulphur, then pour upon the ethiops thus formed, by small portions at a time, the solution of potassa, and stir it. Put the mixture into vessels of porcelain, earthenware, or cast-iron, and heat on a sand-bath at a temperature of from 45° to 50° C. After 7 or 8 hours of such heating, during which the evaporated water has been replaced, the product passes from a black to a brown-red, and lastly to a scarlet-red. When the vermilion has acquired its greatest degree of brightness, it is removed from the fire, then digested for some time at a low temperature, and lastly washed several times, and separated from the uncombined mercury.

C. *Jacquelin Process.*

The proportions of the raw materials are different in this case. Take 90 grammes of mercury, 30 of sulphur, 20 of hydrated potassa, and 30 grammes of water. The mercury and the sulphur are placed in a shallow cast-iron dish, dipping into cold water, and the solution of potassa is added by degrees while the substances are stirred with a large pestle. When all the potassa has been added, the dish is heated at 80° C. for one hour, and the evaporated water is replaced. After that, the vermilion is washed in five or six times its weight of boiling water, and the still hot liquor is decanted with the uncombined and suspended sulphur. Other washings with cold water remove the alkaline sulphides. Lastly, the vermilion is collected upon a filter, drained, and dried.

We see that there is a great analogy between all of these processes, and that, to arrive at a fine quality of vermilion, the success appears to depend upon pure materials, good proportions, and, especially, a proper temperature. Indeed, we know that vermilion loses part of its brightness when it has been overheated.

Mr. Weshle assures us that he can produce a bright vermilion by finely pulverizing cinnabar, mixing it with 1 per cent. of sulphide of antimony, and boiling it several times with 3 parts of sulphide of potassium in a cast-iron pot. The precipitate is then washed with pure water, digested with hydrochloric acid, and washed again. There is nothing surprising in this process, since we know that under certain circumstances the sulphide of antimony acquires a fine red color, as we shall see further on.

D. *Firmenich Process.*

Cinnabar, says Mr. Firmenich, is found in the native state, either in crystals, or compact and earthy crystalline, or fibrous, or pulverulent, etc. It is found in pockets or in veins, or is earthy and mixed with other rocks. It is chemically prepared either by the dry or by the wet way.

In the manufacture of cinnabar, 7 parts of mercury and 1 of sulphur are melted in an iron vessel, and the resulting sulphide is then sublimed in other vases of refractory clay. At Idria, the first mixture is effected in rotary tuns, and the chemical combination and the sublimation take place in heated cast-iron retorts.

A process which is less known, and which gives better results than all of the other methods, in the beauty of the color and the resistance to the fire, is that with the sulphide of potassium. This mode of operation supposes this reagent to be in a great state of purity. There are various methods of preparing it, but we should discard those by which a lye of caustic potassa is boiled with an excess of sublimed sulphur, or when potassa and sulphur are fused together, because there is also formed a hyposulphite or a sulphate of potassa, which comes in the way of the preparation of the cinnabar.

A pure sulphide of potassium is obtained by reducing the sulphate of potassa* with charcoal, and

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* The author employs and repeats the words "sulphide of potassa," which we do not understand, and for which we have substituted those of "sulphate of potassa."—Trans.

saturating the lye afterwards with sulphur to the degree required for the operation.

For instance, 20 parts of sulphate of potassa* and 6 of charcoal are finely powdered, and thoroughly mixed. The whole is then strongly heated in a Hessian crucible, luted and placed in an air furnace. Although not seen, the mixture boils in a lively way, and the crucible should not be filled to more than two-thirds of its capacity. The melted and cooled mass is a simple sulphide of potassium (KS), which presents a crystalline appearance, is colored brown or red, and attracts the dampness of the air. It is boiled in a cast-iron kettle with pure or rain water, in the ratio of 2 parts of substance to 7 of water, and is then filtered. By cooling, the undecomposed sulphate of potassa* crystallizes on the sides of the vessel.

Thus purified, the lye is again boiled with powdered sulphur, which is added by small quantities at a time, until saturation, which is ascertained by the effervescence of the liquor, and the formation of bubbles at its surface. The simple sulphide of potassium, by this saturation, absorbs 4 atoms of sulphur. The contact of the air should be avoided as far as practicable, because its oxygen decomposes the sulphide.

The cinnabar is manufactured as follows: Bottles are filled with 5 kilogrammes of mercury, 1 of sulphur, and 2.25 of the lye of sulphide of potassium, and, after having been moderately heated, they are shaken, two at a time, in a basket hanging from a spring, and striking a straw mattress in its descent.

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* The author employs and repeats the words "sulphide of potassa," which we do not understand, and for which we have substituted those of "sulphate of potassa."—TRANS.

After one and a half or two hours of such motion, the bottles become hot, and the mixture acquires a greenish-brown color. The mercury combines with the sulphur of the lye, while the latter keeps up its degree of saturation from the added sulphur.

In order to keep the mixture in a greater state of division and more porous, it is recommended now and then to turn the bottles. After three and a half hours the mercury is entirely combined, and the mixture is a dark-brown. It is then left to cool off slowly. The whole operation lasts five hours. The bottles are next carried into a stove-room, where the temperature is maintained at from 45° to 50° C., and where the mixture gradually turns red. This heating continues from two to three days, and the contents of the bottles should be well stirred three or four times every day.

The temperature has a decisive action upon the tone of the color; the cooler the mixture before the shaking operation, the lighter will be the color of the product. For instance, a light carmine cinnabar with a yellowish tinge is prepared by cooling the bottles for one hour in the open air, in winter; but in summer they are cooled in water.

It now remains to free the cinnabar from the excess of sulphur, and this is done in the following manner: About 6 decilitres of pure water are added to each bottle, which is shaken and emptied upon a filter. The clear lye runs out, and the remaining cinnabar is put into a stoneware pot, where it is mixed with a lye of caustic soda, which dissolves the remaining free sulphur. Some time afterwards the lye is decanted as completely as possible, and the deposit is washed several times by decantation, and lastly, upon a filter.

The solution of the excess of sulphur, and the washing off of the caustic lye, require a great deal of care. Indeed, the resistance of the product to the action of the fire entirely depends upon the first operation; the second insures the greater or less durability of the color. The filtration takes from two to three days, and the drying is effected at a very low temperature until the cinnabar can be broken to pieces, and is dry to the touch. It is then placed in iron basins, and is repeatedly stirred, while the temperature of the stove-room is raised to 60° or 62° C.

Under the influence of too much heat the cinnabar becomes of a darker color; this is not a defect, since the color becomes more steady when exposed to the fire. This last drying requires about five hours.

As we have already stated, this mode of preparing cinnabar is to be preferred to all others, because the product answers the requirements of beauty of color, and is capable of withstanding fire, the latter quality especially being wanting in most of the other cinnabars. Moreover, the figures prove that this method produces a cheaper cinnabar than those prepared in the usual manner.

Many trials have been made to brighten the color of vermilion and increase its fire. Here are some results:—

Desmoulins, in 1825, employed a lye of caustic potassa. Mr. Dumas, in his *Traité de Chimie*, states that unsuccessful attempts have been made with nitric acid to impart to French vermilion the brightness of that of China. However, the particulars as to the proportion and strength of the acid were not made public. MM. Pelouze & Fremy, in their *Cours de Chimie*, indicate the use of hydrochloric acid for washing the paste of vermilion.

Lastly, it appears from a recent lawsuit that Mr. Ringault, Sr., manufacturer of colors at Paris, took out, on the 15th of October, 1859, a patent for the preparation of a vermilion unalterable by fire. The process consists in a method of purifying and brightening the cinnabar ground in water, so that the resulting vermilion acquires a depth of color and a durability seldom arrived at. Here are the various operations:—

1. Treatment with nitric acid, which removes all the excess of sulphur.
2. Treatment by a hot mixture of sulphide of potassium and caustic potassa.
3. Digestion of the vermilion in hydrochloric acid.
4. Hot treatment of the paste with a solution of caustic potassa, in order to give a more or less violet tinge to the vermilion.

Mr. Desmottes, manufacturer of vermilion at Paris, has tried to imitate this process as follows: The vermilion is treated by nitric acid, with the useless addition of acetic acid. Then comes the employment of a hot solution of potassa, to which powdered sulphur is added. Lastly, the paste is digested with hydrochloric acid. The process is the same as that of Ringault, and produces vermilions possessing the desired qualities of brightness and durability.

Vermilion is quite often adulterated. Its purity may be ascertained by heating it in a closed vessel. The pure article is entirely volatilized, whereas the impurities, such as powdered brick, red lead, red ochre, colcothar, etc., remain on the bottom of the vessel. By a treatment with hot nitric acid a vermilion holding red lead or orange mineral becomes brown. Thrown upon burning coals it emits garlic-smelling fumes if it has been adulterated with realgar.

It is useless to say that cinnabar and vermilion are poisonous colors.

§ 10. *Iodide of mercury.*

The iodide, or rather the bi-iodide of mercury, is a salt possessing a red color of the greatest brightness, but which is rendered yellow, and then black, by the action of light. It is scarcely employed now-a-days, except in water colors. Moreover, it is highly poisonous, and there are several other pigments, which when mixed with it, decompose it.

The preparation of this oxide, which is called *scarlet* in England, is quite easy. Two dilute solutions, one of 80 parts of bichloride of mercury (corrosive sublimate) and the other of 100 parts of iodide of potassium, are mixed together, and the resulting precipitate is washed with distilled water, first in the vessel and then upon a filter, and lastly, dried at a low temperature. This color should be kept in black bottles.

Heller affirms that this bi-iodide becomes more durable if it be dissolved in a hot and concentrated solution of sal ammoniac. By cooling, the color is precipitated in the shape of fine purple crystals, which are washed and finely pulverized.

§ 11. *Chromates of mercury.*

The combination of chromic acid with the binoxide of mercury furnishes, according to Mr. Millon, two chromates which differ in their composition and their color.

The first of these chromates is obtained by pouring a solution of chromate of potassa into a solution of nitrate of binoxide of mercury. A very dark brick-red precipitate is formed, which is washed several times by decantation, and then dried in the air and in the dark.

The other chromate is prepared by boiling for a long time, the red oxide of mercury with a concentrated solution of bichromate of potassa. The precipitate is separated by decantation, washed several times with hot water, and dried in a dark place. When it has been well prepared it has a fine violet tinge.

These colors are costly of production, and are easily decomposed by light.

§ 12. *Chromate of copper. Maroon-red.*

This color is not yet very well known, and is prepared with a boiling solution of sulphate of copper, poured, drop by drop, into another boiling solution of neutral chromate of potassa. There are formed a soluble sulphate of potassa and a precipitate of chromate of copper, which are washed by decantation with hot water until the latter is colorless. It is afterwards collected and drained upon a filter and dried in a stove.

§ 13. *Chromate of silver. Purple-red.*

The chromate of silver is a color without much durability, which is employed only in miniature painting. It is prepared by pouring a solution in distilled water of 30 parts of crystallized nitrate of silver into another solution of 30 parts of neutral chromate of potassa, also in distilled water. The purple-red precipitate is washed with distilled water, then thrown upon a filter, and dried in the dark.

§ 14. *Sulphide of antimony. Vermilion of antimony.*

Lampadius had already, in 1833, proposed for a pigment, the red sulphide of antimony, which covers well when employed with water, but which possesses less body when ground in oil. Since then, several chemists have examined this sulphide for a coloring substance, but we shall mention only those experiments which seem useful in practice.

Mr. E. Mathieu-Plessy has published an interesting memoir on the vermilion of antimony (*Bulletin de la Société industrielle de Mulhouse*, vol. 26, p. 297), from which we give an extract:—

"The product to which I give the name vermilion of antimony, is the result of a new modification of the sulphide of antimony, which I obtain from the decomposition of hyposulphite of soda in the presence of chloride of antimony.

"Among the phenomena of double decomposition, so characteristic of the nature of mineral substances, none is more striking than the production of the orange-yellow sulphide of antimony by means of sulphuretted hydrogen or of an alkaline sulphide. If the latter reagent, from long exposure to the air, be partly transformed into hyposulphite, it may give with a protosalt of antimony, according to its greater or less degree of oxidization, variously colored precipitates. These variations, which may have been observed already, will be easily explained by the reaction which I have studied out, and which gave me the key for obtaining a red sulphide of antimony entirely distinct from the following well known ones:

"I refer to the orange-yellow sulphide produced by the reaction of sulphuretted hydrogen upon the protochloride of antimony—the black native sulphide—and the brown-red sulphide, a modification of the preceding one, which was observed for the first time by Fuchs, and has recently been studied by Mr. Rose.

"It is not sufficient, however, to put the protochloride of antimony and the hyposulphide of soda in contact with each other, to obtain the sulphide of antimony with all the brightness which it is able to acquire. In order always to arrive at the desired result, I have been obliged to make numerous trials, and to vary the proportions of the reagents and the temperature. At last I have succeeded in finding out a process which is satisfactory in regard to the quality of the product and the facility of its preparation.

"Believing that the vermilion of antimony might find its application in the arts, I have examined its preparation from beginning to end, and I have, therefore, aimed to produce the hyposulphite of soda and the chloride of antimony on a manufacturing scale. In regard to the hyposulphite of soda, and in view of avoiding the crystallizations which require a peculiar apparatus, I followed a process which gave me this salt in a state of sufficient purity, at a time when its preparation was but little understood. This process was based upon the employment of the sulphite of soda.

"In my researches I have demonstrated that this salt should be employed in the neutral state, in order to avoid the reaction of the sulphurous acid upon the hyposulphite, resulting in the Langlois salt, which, being also decomposed, becomes sulphate of soda. In the preparation of the sulphite I have followed the process of Mr. Camille Kœchlin, which consists in burning sulphur in an apparatus easily established. There is a sieve holding large crystals of soda, which is suspended in a cask opened at the top. The bottom is connected by means of a pipe with a small clay furnace, upon which the sulphur is thrown by small quantities at a time.

"The combustion of the sulphur is regulated by means of a trap-door; the draft is good, and after two or three days the crystals of soda are transformed. Should there be portions unacted upon, the easily crumbling sulphite is rubbed off, and the core of carbonate is replaced in the cask. A solution marking 25° Bé., is made with the sulphite, and is afterwards heated and saturated with crystals of soda. When the addition of this salt ceases to produce an effervescence (litmus paper does not give sufficient indications), or rather, when a diluted sample of the liquor produces a slight disengagement of carbonic acid by the addition of hydrochloric acid, then sublimed sulphur is put in, and the mixture is heated for three hours upon a water-bath. During that time the evaporated water is replaced, and the mass is frequently stirred. The cold liquor is diluted with water, so as to mark 25° Bé.

"The protochloride of antimony is easily prepared by boiling in hydrochloric acid the powdered native black sulphide of antimony. When the disengagement of hydrosulphuric acid begins to be slow, the whole is made to boil for a few minutes. After cooling, the clear liquid is decanted.

"In order to obviate the inconvenience of the production of sulphuretted hydrogen, the gas is collected in a solution of soda, or it is burned at the end of a glass tube connected with the vessel, where the reaction takes place. If a burning alcohol lamp be placed at the end of the tube, the combustion of the gas will not be arrested, even should the gas be accompanied by a large proportion of steam. The chloride of antimony thus obtained is diluted with water to 25° Bé.

"The two solutions of antimony and of hyposulphite being prepared, we proceed as follows: We pour into a stoneware vessel 4 litres of chloride of antimony, 6 litres of water, and 10 litres of hyposulphite of soda. The precipitate caused by the water is rapidly dissolved, in the cold, by the hyposulphite. The vessel is then placed in a hot-water bath, where the temperature of the mixture is gradually raised. At about 30° C. the precipitate of sulphide begins to form; it is orange-yellow at first and becomes darker afterwards. At 55° C. the vessel is removed from the water bath, and the precipitate is allowed to settle, which it does rapidly. The mother liquors are decanted, and the deposit is washed the first time with water holding $\frac{1}{15}$ of hydrochloric acid, and afterwards with ordinary water. Lastly, the precipitate is collected upon a filter and dried. The wet vermilion of antimony is of an exceedingly bright red color; after drying it loses part of its brightness. This pigment may be prepared in the cold, but the product is finer and more constant if we operate in the manner just described.

"Being certain to reproduce my new sulphide whenever it is desired, I have undertaken its analysis. But as the determination of the antimony is very difficult, and as there is no known method sufficiently accurate for the purpose, I have determined the sulphur and calculated the antimony by difference. It has also been necessary to determine the proportion of water. Moreover, I have compared the orange-yellow sulphide with my own, and the result is—

0.668 of orange-yellow sulphide lose	0.038 at 200° C.
0.808 of red sulphide lose . .	0.009 at 200° C.

"This proves that the vermilion of antimony is an anhydrous substance, the above loss being evidently due to an imperfect drying.

"There now remains to prove by analysis, that the vermilion of antimony differs from the orange-yellow sulphide by only one equivalent of water. This explains the new properties of the red sulphide. I have found by analysis—

Water	1.1
Sulphur	26.7
Antimony (by difference) . .	72.2
	100.0

which composition proves that the equivalents of sulphur and antimony are in the ratio of 3 to 1."

M. E. Kopp has also published, in the *Bulletin de la Société Industrielle de Mulhouse*, vol. 20, page 379, a memoir on the manufacture of the vermilion of antimony. We reproduce the following extracts:—

"The sulphide of antimony, according to its physical state and its mode of preparation, may present very varied colorations. It is crystalline and blackish-gray in the native state and melted. Kept in the molten state for a long time, and suddenly cooled, it becomes hyacinth-red. Precipitated by sulphuretted hydrogen from an antimonic solution, it is of an orange color more or less red. In the kermes state it is red-brown. Lastly, obtained from the reaction of a soluble hyposulphite upon the chloride of antimony, its red color is more or less bright, and more or less orange or crimson, in accordance with the temperature employed, and the concentration of the liquors.

"This latter reaction was indicated by several chemists, who gave recipes for the regular manufacture of the fine red sulphide of antimony, which was called *vermilion of antimony.*

"All of these methods are based upon the employment of hyposulphite of soda and chloride of antimony in quite concentrated solutions, and they present various inconveniences.

"In the process which I have followed, the vermilion of antimony is obtained by the reaction of the chloride of this metal upon a dilute solution of hyposulphite of lime; and the mother liquors are used several times, and are thrown away only after they contain too great a proportion of chloride of calcium.

"I am now going to describe successively the various operations in the manufacture of the red sulphide of antimony.

"1. *Preparation of the Chloride of Antimony.*—The decomposition of the sulphide of antimony by hydrochloric acid, is very easy in experimental laboratories, but the operation presents great difficulties when we have to work upon large quantities of materials.

"After a series of experiments (employment of leaden vessels, heating of stoneware vessels in sand and pitch baths, etc.), I found that it was much better to roast the sulphide of antimony at a moderate temperature, and with the contact of air and steam. The greater part of the sulphide is transformed into oxide of antimony, and the sulphurous acid produced is used in the manufacture of the hyposulphite of lime. The oxide of antimony is then easily dissolved in commercial hydrochloric acid.

"If, during the oxidation of the sulphide of antimony, there is produced a certain proportion of antimonious acid, but slightly soluble in hydrochloric acid, it may be saved by collecting the residues from the treatment with hydrochloric acid, and washing them with chloride of calcium or hyposulphite of lime, which dissolves the adherent chloride of antimony. They are then dried and melted with a certain proportion of sulphide of antimony and of quicklime, in order to transform the whole into antimony green. The addition of a small quantity of quicklime is intended for decomposing the small proportion of chloride of antimony which may still remain in the residues.

"2. *Preparation of the Hyposulphite of Lime.*—This salt is cheaply prepared by the action of sulphurous acid upon the sulphide or polysulphide of calcium, or the oxysulphide. The sulphurous acid is produced by the combustion of brimstone, or the roasting of pyrites, or of sulphide of antimony.

"The polysulphide of calcium is prepared by boiling finely ground sulphur with newly slaked lime and a sufficiency of water. It is advantageous to add to this solution of polysulphide, a certain proportion of powdered oxysulphide of calcium, which is the residue of the lixiviation of crude soda. In the absence of oxysulphide, quicklime may be added.

"Sulphurous acid, in its reaction upon the sulphide and the oxysulphide of calcium, sets sulphur free, and forms a sulphite of lime, which, in presence of the sulphur and of the undecomposed sulphide, is soon transformed into hyposulphite of lime. The reaction is aided by the elevation of temperature which takes place in the apparatus.

"The liquor is examined now and then to see whether it is alkaline, neutral, or acid. As soon as it has become slightly acid, it is run from the apparatus into a large settling tank, where it generally becomes neutralized by a certain quantity of undecomposed oxysulphide of calcium held in it. If, after stirring for some time, the liquor preserves its acid reaction, sulphide of calcium is added until complete neutralization, which is ordinarily made apparent by a black precipitate of sulphide of iron.

"After settling for some time, the clear liquid is decanted, and forms a solution of nearly pure hyposulphite of lime. The same vessel is subsequently used for neutralizing the liquors obtained during the process of manufacture.

3. "*Preparation of Vermilion of Antimony.*—The red sulphide of antimony is prepared with the above solutions of chloride of antimony and of hyposulphite of lime.

"The apparatus is simply composed of several wooden tanks, holding from 20 to 30 hectolitres each, and raised about 1 metre above the floor. These tanks are so arranged that they may be heated by steam, either through a copper or lead pipe, the opening of which is about 2 decimetres from the bottom, or, what is preferable, through a coil of pipes, the condensed steam of which may be carried outside, without being mixed with the liquors. In this manner we avoid the useless dilution of the liquors producing the vermilion of antimony.

"When the pressure of the boilers has reached two or three atmospheres the tanks are filled with the solution of hyposulphite of lime up to seven-eighths of their height. We then pour the solution of chloride of antimony into the first tank, 2 or 3 litres at a time. There is formed a white precipitate which is rapidly dissolved at the beginning, but when it becomes slow of solution, even by stirring the liquor, the addition of chloride of antimony is discontinued, because there must always be a certain excess of hyposulphite of lime.

"The liquor of the tank should be perfectly clear and limpid, and any white precipitate should be dissolved by adding small quantities of hyposulphite.

"Steam is then let in, and the temperature of the liquors is gradually raised to 50° or 60°, or even 70° C., while stirring goes on. The reaction soon becomes manifest; the liquid is successively colored a straw-yellow, then a pure lemon-yellow, orange-yellow, orange, reddish-orange, and lastly, a very deep and bright orange-red. The steam is then stopped, and the acquired heat of the liquid, aided by a slow stirring, is sufficient to complete the reaction, and impart to the color its maximum of intensity. Should the heating be continued, the red-orange color would pass successively to a pure red, then to a more or less crimson red, which in its turn would grow darker and darker, and become brown, blackish-brown, and, lastly, nearly black.

"We see that by graduating the temperature it is possible to obtain all the intermediate hues between orange and brown-black. The tank is covered, and the colored precipitate is allowed to deposit.

"The clear and limpid liquor, which smells strongly of sulphurous acid, is decanted through holes bored in the tank at different heights, and is conducted by means of leaden pipes or wooden troughs into a large reservoir holding a certain quantity of sulphide and oxysulphide of calcium. The sulphurous liquor regenerates a certain proportion of hyposulphite of lime.

"As the solution of chloride of antimony always contains a large proportion of chloride of iron, it becomes easy to watch the working of this latter operation. All the iron remains soluble in the mother liquors of the sulphide of antimony, and as soon as they are brought in contact with the sulphide of calcium, there is a formation of insoluble sulphide of iron. As long as the black precipitate remains, the mother liquors charged with sulphurous acid have not been added in excess. But when they are in excess the black precipitate disappears, since it is transformed into a soluble hyposulphite of iron. The contents of the reservoir are then well stirred, and, if necessary, sulphide of calcium is added, until the black precipitate of sulphide of iron reappears and remains permanent. At the same time a certain proportion of hyposulphite of iron should remain in solution. This condition is easily fulfilled when we operate upon a sufficiently large amount of materials. After the precipitate has settled the liquor is decanted, and is a neutral solution of hyposulphite of lime, with a certain proportion of hyposulphite of iron and of chloride of calcium.

"We should carefully avoid, in this regeneration of the hyposulphite of lime, leaving in an excess of sulphide of calcium, which will impair the coloration of the vermilion by causing the formation of the ordinary orange-yellow sulphide of antimony. Therefore, if the solution of hyposulphite of lime be yellow and alkaline, a liquor charged with sulphurous acid should be added, until complete neutralization of the alkaline reaction.

"This solution of hyposulphite of lime, like the first, is employed in the preparation of a new quantity of vermilion of antimony. The mother liquors, charged with sulphurous acid, are again neutralized in the large reservoir by a new proportion of sulphide and oxysulphide of calcium, and so on, until the liquors become so much loaded with chloride of calcium that it becomes necessary to throw them away, or to reserve them for some other purpose. But this takes place only after twenty-five or thirty operations.

"It is even possible to save the sulphurous acid of these worn-out mother liquors, by saturating them with a milk of lime. There is a precipitate of oxide of iron and of sulphite of lime, and the mother liquors contain only chloride of calcium. The precipitate, mixed with sulphide of calcium, is transformed by sulphurous acid into the hyposulphites of lime and iron. And if the proportion of iron be too great, it may be precipitated by a slight excess of a milk of lime.

"The precipitate of vermilion of antimony left on the bottom of the first tank is received into a conical cloth filter, and the drained liquors are added to those of the reservoir. The tank is then rinsed with tepid water, which is made to pass through the filter.

"The washing of the vermilion should be done very carefully, and it is often necessary to empty the contents of the filter into a large volume of pure water, and to wash several times by decantation. The red sulphide is afterwards filtered again and dried at the ordinary temperature, or in a stove-room, the temperature of which is not over 50° to 60° C.

"While the precipitate is settling in the first tank a similar operation takes place in the second, and then in the third. During that time the first tank has been emptied, and its mother liquors have been regenerated. These are then brought back into the first tank, and another precipitation of vermilion of antimony takes place, and so on.

"We see that by this process the expense in sulphur, and therefore in sulphurous acid and hyposulphite, is reduced to a minimum.

"4. *Properties of the Vermilion of Antimony.*—The vermilion of antimony is in the state of a very fine powder, without taste or smell, and is insoluble in water, alcohol, or essential oils. It is but little acted upon by the weak acids, even concentrated; or by the powerful inorganic acids which have been diluted with water. It stands the latter acids better than the ordinary sulphide of antimony. Concentrated and hot hydrochloric acid dissolves it, when sulphuretted hydrogen and chloride of antimony are formed. Nitric acid oxidizes it, with production of sulphuric and antimonic acids. The vermilion of antimony is not sensibly acted upon by ammonia or the alkaline carbonates; on the other hand, the powerful caustic alkalies, such as potassa, soda, baryta, strontia, and lime, decompose it and form combinations which are colorless, or nearly so. The color is therefore destroyed, and thus we see that this pigment should not be mixed with alkaline substances. A high temperature blackens it, and should the heat be such as to melt it, it becomes ordinary sulphide of antimony.

"The vermilion of antimony is an opaque color, without much lustre or brightness, when it is mixed with water, thickened by gummy or gelatinous substances. On the other hand, when ground in oil or varnishes, it acquires a great intensity and brightness of color, and has a good body or covering power, being superior in that respect to red lead, orange mineral, the red subchromate of lead, and cinnabar or vermilion with a basis of mercury. A well-prepared vermilion of antimony, ground in oil, gives possibly the purest red color, that is to say, it is not tinged orange, or pink, or crimson; but it often has a brownish hue. It is perfectly unalterable by air or light, and may be mixed with white lead, which is not blackened by it, even after several years. It does not assist or hinder the drying of oil. Therefore, the vermilion of antimony is a pigment especially fitted for oil painting, and its low price and covering power render it advantageous for carriage and house painting."

§ 15. *Sulpho-antimonite of barium.*

Mr. R. Wagner has indicated the sulpho-antimonite of barium, combined with the artificial sulphate of baryta (blanc fixe), as furnishing good pigments for painting.

The sulpho-antimonite of barium is prepared by mixing—

Finely powdered sulphate of baryta . . .	2 parts.
Native gray sulphide of antimony	1 part.
Powdered charcoal	1 "

and calcining the mixture at a red heat for several hours in a crucible of clay or graphite. The crucible should not be opened before it is entirely cold, because the carbonaceous mixture easily becomes inflamed. The calcined mass is then boiled in water, and, as the insoluble residue still contains undecomposed sulphate of baryta and sulphide of barium, it is mixed with the materials of another operation.

The filtered liquor is a pale-yellow, and dilute sulphuric acid is added to it until the orange color is entirely precipitated. Sulphuretted hydrogen is disengaged.

The color is diluted with blanc fixe. If a purer orange hue be desired, the solution of sulpho-antimonite of barium is boiled with $\frac{1}{5}$ part of sublimed sulphur. The sulpho-antimonite of barium is transformed into sulpho-antimoniate, which has a composition analogous to Schlippe's salt. If the liquor, filtered from the undissolved sulphur, be precipitated by sulphuric acid, we obtain a mixture of blanc fixe and persulphide of antimony. As during the boiling of the liquors a part of the sulphide of barium is transformed into polysulphide, there is always in the precipitate a small proportion of sulphur, which is said to be productive of no inconvenience.

Instead of the ordinary sulphide of antimony the vermilion may be mixed with the sulphate of baryta. The mixed pigment will be obtained at once by employing sulphuric acid for the decomposition of the hyposulphite of soda, which has previously been mixed with the chlorides of antimony and barium.

§ 16. *Cobalt pink.*

Cobalt pink is a mixture of the oxide of this metal with magnesia. It is a durable color, and more or less pink, according to the proportion of cobalt it contains. It is an expensive pigment, which is used only for fine painting. Its preparation consists in making a paste of carbonate of magnesia with a concentrated solution of nitrate of cobalt. The paste is dried in a stove, and then calcined in a porcelain crucible.

§ 17. *Arseniate of cobalt, metallic lime.*

This salt is employed in oil painting, possesses a very deep and durable red hue, and is found native in cobalt mines combined with other substances. These are removed by a treatment with boiling nitric acid, which dissolves the pigment and the other impurities. The clear liquor receives small additions of potassa until all of the iron is precipitated as arseniate; then, after settling and decanting, a further addition of potassa precipitates the arseniate of cobalt.

For preparing the artificial arseniate the sulpho-arsenide of cobalt (gray cobalt) is powdered, mixed with a little sand and twice its weight of potassa, and then fused in a crucible. There is produced a kind of cinder of sulphides, which is removed. The remaining white arseniate of cobalt is pulverized and again fused with potassa. The new cinders formed are removed, and the button of pure arsenide is powdered and roasted, in order to transform it into the arseniate, the deep-red color of which is still brightened by fine grinding.

§ 18. *Purple of Cassius.*

This substance, which bears the name of its inventor, is the precipitate which takes place when solutions of gold and chloride of tin are mixed under proper conditions. The preparation of the purple of Cassius is quite difficult, and we shall explain it in extenso, in order that good results may be obtained. We should observe that a pure and neutral solution of protochloride of tin, mixed with another solution of neutral chloride of gold, produces maroon, brown, blue, or green precipitates, and sometimes metallic gold, according as the liquors are more or less concentrated. The bichloride of tin does not produce a precipitate with the solution of gold; but the reunion of the two chlorides occasions a precipitate of a purple color. Oberkamps has observed that the hue is the more violet as the proportion of chloride of tin is greater than that of gold; and, conversely, that the hue is pink if gold be in excess.

Buisson recommends the following process for obtaining a fine purple: A neutral solution of protochloride of tin is prepared by dissolving 1 part of tin in hydrochloric acid. On the other hand, 2 parts of granulated tin are dissolved in an aqua regia composed of 3 parts of nitric acid and one of hydrochloric acid, and the excess of acid removed. Lastly, 7 parts of gold are dissolved in an aqua regia made of 1 part of nitric acid and 6 of hydrochloric acid, and just enough, and no more, of this mixture should be employed for obtaining a neutral solution. The solution of gold is diluted with 3½ litres of water, receives the solution of bichloride of tin, and then the protochloride of tin is poured in, drop by drop, until the precipitate has acquired the desired color. An excess of protochloride of tin imparts a bluish hue. After settling, the precipitate is rapidly washed by decantation, and dried in the dark.

Buisson ascertained that a sample of purple, prepared by this method, was composed of—

Metallic gold	285
Bioxide of tin	659
Chlorine	52
Loss	4
	1000

Oberkamps has found—

	In violet purple.	In light purple.
Gold	0.398	0.795
Oxide of tin	0.602	0.205

Berzelius has obtained from a purple of good quality—

Gold	0.2835
Bioxide of tin	0.6400
Water	0.0765
	1.0000

It is difficult from these analyses to arrive at a conclusion as to the composition of the purple of Cassius. In a more recent course of study Mr. L. Figuier has demonstrated that this substance is a stannate of protoxide of gold, which may be obtained of a constant composition by the following process:—

The bichloride of gold is prepared by dissolving 20 grammes of gold in 100 parts of aqua regia, made with 4 parts of hydrochloric acid and 1 of nitric acid. The solution is evaporated to dryness in a water-bath, in order to expel the excess of acid, and the remaining chloride of gold is dissolved in 750 grammes of water. Pure granulated tin is then introduced into the filtered liquor, which, after some time, becomes brown and turbid. After standing several days all the gold is in the state of stannate of protoxide, which is separated from the remainder of the metallic tin. The product is collected upon a paper filter, carefully washed, and dried at a gentle heat.

If the purple remains in suspension in the liquor, it is made to settle by the addition of common salt, and a slight heating.

The separation of the metallic tin, by decantation, should be done carefully, because there is a black tin powder which settles before the purple. This powder, which contains gold, is collected apart for another operation.

The purple of Cassius is extensively used for painting on porcelain; it is also employed in miniature painting.

§ 19. *Madder lake.*

Madder is the name of the ground root, and *alizari* that of the whole root of a plant (*Rubia tinctorum*), which was formerly imported from the East and from Holland, but which is now successfully cultivated in several French departments.

We shall not in this work try to give all the characteristics by which the madders from Holland, Avignon, and the East are recognized. We neither believe that it is of advantage to indicate the various trade-marks, because these marks have become quite illusory. The best is to trust to respectable persons, well acquainted with that product, or to learn one's self how to recognize the characteristics, types, and qualities of the various madders found in the trade.

Madder and garancin are often adulterated with various substances, the powder of tinctorial woods, for instance.

Among the processes generally employed for ascertaining the presence of the coloring substances added to madder or garancin, there are but few which do not require a good knowledge of chemical manipulations. It is very difficult, sometimes, even for persons conversant with these manipulations, to determine with certainty the nature of the foreign substances, especially when the adulteration consists of a mixture of various coloring woods. Mr. J. Pernod, of Avignon, has communicated to the *Société Industrielle de Mulhouse*, the following simple and practical processes:—

The vegetable powders or their extracts, employed for the adulteration, may be divided into two classes: the first comprises all of the tinctorial woods which will form colored compounds with alumina and the oxide of iron; such are the woods of Brazil, Campeachy, Cuba, etc.

The second class comprises all of the substances holding more or less tannin, with or without coloring matter. These substances do not make colored compounds with alumina, but they form brown or black precipitates with the oxide of iron.

In order to detect in madder or garancin the addition of a small proportion of the various coloring woods of the first class, a piece of white paper, from 10 to 15 centimetres square, is dipped for about one minute into a solution of bichloride of tin.* It is then spread upon a plate or a sheet of glass, and dusted over, by means of a sieve, with 1 or 2 grammes of the powdered sample. After half an hour, all the points touched by the particles of foreign woods will present the following colorations: crimson red spots with Brazil wood; violet with Campeachy; yellow with

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* This is the tin-bath of the dyers, obtained by dissolving 10 parts of tin in a mixture of 25 parts of nitric acid and 55 parts of hydrochloric acid. This liquor, for use, should be diluted with twice its weight of water.

Cuba wood, etc., while the portions of the paper in contact with the madder will be slightly yellow.

The substances of the second class are detected in this manner: a piece of writing paper is immersed in an old bath of protosulphate of iron, part of which has been peroxidized, or in a fresh one to which a few drops of neutral nitrate of iron have been added. After being dried, the paper is moistened uniformly with a small quantity of alcohol (87 or 88 per cent.), and then placed upon a sheet of glass. A *very small quantity* of the suspected powder is dusted over it by means of a fine silk sieve, which is kept very near the paper, in order not to lose by a current of air any particle of the foreign matters, which are generally finer than the madder. After a quarter of an hour of contact, there are blue-black spots on the points touched by the adulterating powder, while the coloration occasioned by madder is rust-like or a light-brown. When the alcohol is entirely evaporated, the dust adhering to the paper is rapidly removed with water, and the blue-black spots due to the combination of the tannin with oxide of iron, become still more apparent.

Madder does not entirely abandon its red coloring principle to cold or hot water; but if a small proportion of alum be added, an intense red solution is obtained, which, with alumina, may produce a handsome red lake.

1. *Robiquet and Colin Process.*

Robiquet and Colin have indicated the following process: 2 kilogrammes of madder are macerated several times in cold water, and pressed each time. They are then heated for three hours upon a water-bath, with a solution of 1 kilogramme of alum in 12 litres of water. After filtration, the liquor receives gradual additions of a solution of pure carbonate of soda, until the precipitation is complete; but the first portions of the precipitate are collected apart, because they are finer. All the precipitates are washed until the decanted liquors have no longer an acid reaction; they are then drained upon a filter, moulded into troches, and dried in the open air, in a place where there is no dust.

2. *Persoz Process.*

The madder is fermented or washed with water containing a small quantity of sulphate of soda. It is then treated for 15 or 20 minutes with ten times its weight of a boiling solution of alum holding one-tenth of alum. The liquor is strained through a filtering bag, and when its temperature has been lowered down to 35° or 40° C., it is neutralized with carbonate of soda. As soon as cubic alum has been formed in the liquors, these are brought to a boil, and there is formed a precipitate of a tribasic sulphate of alumina, which carries down with it all the coloring matter. The lake thus produced is carefully washed. This lake, in the opinion of Mr. Persoz is superior to all others on account of not being gelatinous, and being therefore easily deposited, washed, and collected. Moreover, it possesses the great advantage for dyeing and calico printing, of being quickly dissolved in acetic acid.

The madder is not entirely exhausted by this operation, and it may be treated a second and a third time with alum. The resulting liquors are generally reserved for working madders which have not yet been submitted to the action of alum-water. But, if lakes be precipitated from them, only one-half, or even one-third, of the carbonate of soda necessary to saturate the alum, should be added.

The liquors from which the tribasic sulphate of alumina has become precipitated, should not be thrown away. They are used boiling for dissolving the coloring matter which may remain in madder or its residue. When charged with coloring principles, they are again saturated and boiled, and a new quantity of colored lake is thus obtained.

In all dye-works, the whole of the coloring principles of madder are not extracted, and there are always valuable residua which may be worked by the Persoz process, or by other methods. But, in such cases, it is not necessary to ferment the madder, or to wash it with sulphate of soda.

Mr. Persoz has also indicated another mode of preparing madder lake, which has been utilized as we shall see further on. For the saturation of the alum liquor, he replaces the carbonate of soda by an equivalent proportion of acetate of lead, the base of which is immediately precipitated as an insoluble sulphate. The lake thus obtained is remarkable for the purity and the intensity of its color.

3. *Lefort Process.*

Mr. J. Lefort, in his *Chimie des Couleurs*, has described the following process for preparing a very fine madder lake:—

"During the year 1827, Robiquet and Colin discovered that by treating madder with two-thirds of its weight of concentrated sulphuric acid, there was produced a blackish carbonaceous substance, in which all the red coloring principle remained unaltered. This substance is now common in the market, under the names of *garancin* and *sulphuric charcoal of madder*. Its coloring power is three times that of the good qualities of madder; therefore it has been almost entirely substituted for the root in print works.

"We have had occasion to employ garancin in the manufacture of lake, and with the following results:—

"1 kilogramme of garancin, 2 kilogrammes of alum, and 18 litres of pure water are boiled for 15 to 20 minutes in a well-tinned kettle. After filtration, and in the still hot liquors, a solution of carbonate of soda is added until the decoloration is complete. By collecting the precipitate at different periods, the lake obtained at the beginning of the operation is finer than towards the end. After a rest of several hours, the clear liquid is decanted, and the lake is thoroughly washed until the water runs out perfectly clear and tasteless. The precipitate is then collected upon cloth filters of a close texture, drained, moulded in troches, and dried in the shade.

"We have every reason to believe that the greater part of the fine madder lakes employed in painting are manufactured from garancin. With ascertained, but variable proportions of garancin, alum, and water, we may precipitate lakes ranging in color from a light pink to a deep red."

4. *Khittel Process.*

Mr. J. Khittel, who has made a special study of the preparation of madder lakes, has indicated in the *Technologiste*, vol. 20, p. 340, a process for the preparation of a purple madder lake, which we reproduce here.

"There are many methods and recipes for preparing lakes with madder, garancin, alizarin, etc.; but I do not believe that they will produce an article which will be satisfactory in every respect, because in the greater number of these methods, there are erroneous manipulations, which have a disastrous influence on the quality of the product, and diminish its value. I have undertaken a series of experiments on this subject, and I hasten to communicate the results.

"The first condition in the preparation of a lake, is to avoid the boiling of madder or any of its solutions, because there are formed products of decomposition, and the lake itself is wanting in brightness. In the preliminary treatment of the raw material (madder or garancin), we should also eliminate as completely as practicable the extractive matters and a yellow substance, which is very prejudicial. The dissolving agent for the coloring principle is generally alum, and rightly so; the alum solution should be employed hot, although never boiled with madder or garancin. I have several times treated a sample of the latter substance with a hot solution of alum, while another portion of the same sample was boiled with the same alum solution. In every case, the lake obtained by ebullition was inferior to that resulting from the first mode of operation.

"Another mistake in the preparation of these lakes, is too great a proportion of alum. As the formation of a lake is based upon the elimination of the alumina, it naturally follows that the greater the proportion of alumina in the liquor, the more earthy and the less bright will be the lake. The best proportion appears to be equal weights of alum and madder or garancin. I entirely discard the employment of soda, potassa, and alkalies, by which the alumina is precipitated in the hydrated state. This use of alkalies will never result in a satisfactory lake, because the alkali itself modifies the coloring substance, and the lake always has a violet tinge.

"Mr. Persoz has obtained a fine lake by adding to the solution of alum a solution of subacetate of lead, then filtering, and boiling the clear solution. I have ascertained that this process is the best, and that, with the proper care during the operation, satisfactory results in quality and quantity will be obtained. Nevertheless, I have made the following modifications:—

"Since the red coloring principle of garancin (rubiacin and alizarin of Higgin) is scarcely soluble in cold solutions of the alkaline sulphates, I begin to purify the garancin with solutions of the crystallized sulphates of potassa or of soda. The proportions which I have found the most satisfactory are—

Garancin	1 kilogramme.
Crystallized sulphate of soda . . .	1 "
Water	36 litres.

"The garancin is put into the water, and remains there for twelve hours. It is then filtered, pressed, and again put into pure and cold water, and these operations are repeated until all the sulphate of soda is expelled, that is, until the washings do not occasion any turbidity in a solution of subacetate of lead.

"A quantity of alum corresponding with that of the garancin to be treated, is dissolved in from ten to twelve times its weight of water, and boiled. The washed garancin is then introduced into the boiling solution, which is removed from the fire. A good proportion is 1 kilogramme of alum, 1 of garancin, and 18 litres of water. After standing for fifteen or twenty minutes the solution is filtered, and the residue of garancin is washed with boiling water. When the temperature of the colored extract has fallen to 45° or 50° C., there is added to it a quantity of subacetate of lead equal to that of the alum employed, and the mixture is stirred until all the subacetate is transformed into sulphate of lead. The colored solution should not be allowed to become cold, because part of the color might be precipitated. After settling, the red and clear liquor is easily decanted from the heavy precipitate of lead.

"But, as this lead precipitate contains always a small proportion of coloring matter and of acetate of alumina, it may be washed with hot water, which may be used for dissolving the alum in a subsequent operation. In such case, the following proportions will be used for 1 kilogramme of garancin already treated once:—

Alum	1 kilogramme.
Subacetate of lead	1 "
Water	18 litres.

"The residue of washed garancin may be submitted to a second similar treatment, but the proportions should be modified as follows per kilogramme of garancin:—

Alum	750 grammes.
Subacetate of lead	750 "
Water	15 litres.

"Should the residue of garancin, after this second treatment, contain enough of coloring matter to cover the expense of a third treatment, we should employ for each kilogramme of garancin twice treated:—

Alum	500 grammes.
Subacetate of lead	500 "
Water	12 litres.

"By heating for some time nearly to the point of ebullition, but without violent boiling, the red solution separated from the lead precipitate, there is separated a purple-red lake which is much superior, in intensity and brightness of coloration, to all the lakes which I have prepared by the other methods. The acetic acid of the liquors prevents the complete precipitation of the alumina and coloring matter. Therefore, after the first lake has been collected, the clear liquor is divided into two equal portions; into one of them a solution of carbonate of ammonia is poured drop by drop, until there is formed a slight turbidity, but not a precipitate. The two portions are then mixed and heated as before, and another quantity of lake is obtained, which, however, is not so bright as the former.

"These two kinds of lake are easily collected and washed upon a filter, and they should be dried at a very moderate heat. An excess of alkaline lye dissolves the wet lake, and becomes colored a violet-red. It is also dissolved in concentrated acetic acid, and the residue of its calcination upon platinum foil is a white-ash of alumina."

5. *Lake of Garanceux.*

By the known processes of dyeing, and when ordinary madder is employed, only from 35 to 40 per cent. of its coloring matter are utilized. The residua are therefore very rich, and of late years have been used for the preparation of a substance called *garanceux.* Several methods have been proposed, but we shall reproduce here only that published by MM. Thierry-Mieg and Schwartz, of Mulhouse.

After dyeing, the madder-bath is mixed with dilute sulphuric acid, and is run out into a filter. The proportions are: 3 kilogrammes of sulphuric acid at 66° Bé. for 400 kilogrammes of madder used. The filter, which may be a pit holding a layer of 20 centimetres of gravel covered with packing cloth, retains the coloring matter precipitated by the acid. The liquor escapes by the bottom, which is also covered with packing-cloth. The residua are collected and put into a vessel with 20 parts of water, and 10 parts of sulphuric acid at 52° Bé., for 100 parts of residua. Steam is admitted into the mixture, which is boiled from four to six hours. After filtration, the residue is washed five or six times consecutively by decantation. It is then saturated and macerated for one hour with a solution of 1 to 2 kilogrammes of crystals of soda, and poured again upon a finer filter. The saturation is complete when a drop of the mixture, being deposited upon a white cloth, produces a slightly pink ring. The garanceux remains upon the filter, and after being pressed, dried, and pulverized, it may be used again in dyeing.

Should the garanceux be submitted to processes similar to those employed for madder and garancin, it seems easy to prepare from it madder lakes.

According to their purity, the mode of preparation, or the adulterations, there are in the market many kinds of madder lakes, the color of which varies from a light pink to a purple or brown, with all the intermediary hues. The substances generally employed for adulterating madder lakes, are the lakes of carmine and of red woods.

6. *Sacc Process.*

Mr. Sacc has prepared very fine lakes from the pasty alcohol extract of madder. Take—

Pasty extract	100	grammes.

and add

Caustic ammonia	50	"
Water	125	"

Macerate for twenty-four hours, and add the same quantity of water as above. Pass through a silk sieve, and add while stirring a boiling solution of 100 grammes of alum in one litre of water. This lake is of a magnificent deep red. By substituting for the alum 125 cubic centimetres of a solution of sulphate of sesquioxide of iron, marking 40° Bé., a deep-violet lake is obtained.

7. *Kopp Process.*

Mr. E. Kopp prepared madder lakes by a process of his invention, and which we shall describe briefly.

The root is powdered coarsely, but uniformly. A solution of sulphurous acid is then prepared by the combustion of brimstone or of pyrites, or by the decomposition of sulphuric acid upon charcoal. In the latter method from 6 to 8 kilogrammes of sulphuric acid produce enough of sulphurous acid for a solution in 10 hectolitres of water.

This solution holds from four to five and a half thousandths of sulphurous acid. If the water be pure, from a half to one-thousandth (in volume) of commercial hydrochloric acid is added to saturate the small proportion of earthy carbonates contained in certain kinds of madder, that of Alsace for instance. On the other hand, calcareous waters require a larger addition of hydrochloric acid in proportion to the quantity of carbonate of lime present.

The madder is mixed with ten times its weight of sulphurous solution, and the whole is left to macerate from twelve to twenty-four hours in wooden tanks, well closed. The mixture is stirred now and then. The semi-fluid substance, with the rinsings of the tub, is then poured into cloth filters, which, after draining, are gradually but strongly pressed. The clear liquor is received in a closed wooden vessel. The pressed madder powder is removed from the filter, and again treated with ten times its weight of the sulphurous solution. The filtered liquor is added to that of the first treatment. Lastly, the residue of madder is mixed for the third time with ten times its weight of sulphurous solution; but as the resulting liquor is poor it is reserved for the second sulphurous treatment of another portion of madder.

The madder is then washed with boiling water, pressed, and dried. It then constitutes a weak "flower of madder," which, however, will produce hues of pure color, and will leave the body ground perfectly white. It may be left wet and converted into a weak garancin by processes indicated by Mr. Kopp.

In order to prepare the lakes of alizarin and purpurin, which are, in the opinion of this chemist, the only valuable coloring principles of madder, the above sulphurous solution is employed.

By adding to this solution small quantities at a time of acetate or hyposulphite of alumina, or of alum neutralized by carbonate of soda, and keeping the bath, however, with an acid reaction, and hot, we obtain successive precipitates of aluminous lakes, which present the following characteristics:—

First lake: Dark red and very bright;
Second lake: Light red and pleasing brightness;
Third lake: Pink, quite pure;
Fourth lake: Pink, slightly yellowish.

The concentrated mother liquors are of a dark-yellow color, and dye a cloth a yellow, somewhat fawn-colored. Therefore, in the opinion of Mr. Kopp, it results that the liquor contains the fawn-colored or yellow principle of madder, after the precipitation of alizarin and purpurin.

Madder lakes are employed with water or oil, and their greatest consumption is for miniature painting and calico printing.

8. *Adulteration of Lakes.*

We have already given some information as to the manner of testing adulterated madders; but, more recently, Mr. T. Chateau, in a memoir on the adulterations of madder and its derivatives, which received a premium from the Chamber of Commerce of Avignon, has indicated the following processes for the detection of the adulterations:—

"Madder lakes are falsified according to their color. When *red* or *pink* the adulteration is effected with lakes from Brazil woods. The *violet carmine lakes* are adulterated with Prussian blue and the lakes of alkanet and Campeachy. *Black* madder lakes are often mixed with the black lakes of logwood, cochineal, sumac, galls, etc.

A. *Red and Pink Lakes.*

"These lakes do not color either hot or cold water. They color alcohol and ether very slightly, and only after a certain length of time. By calcination they leave a white residue of alumina.

"*Santaline.*—If the lake be dark it may contain santaline, which is detected by the *orange-red* color acquired by the ether digested with the suspected lake. Alcohol, under the same circumstances, would be colored red.

"If the lake be of a pink hue it may be falsified by lakes of Brazil wood or of cochineal. But as madder lakes, and generally all lakes, are insoluble in water, ether, or alcohol, their coloring substance should be insulated, and I propose the following method:—

"Every lake with alumina for base is soluble in hydrochloric acid, or in acetic acid to which a few drops of the former acid have been added, or in a solution of protochloride of tin. After the lake is dissolved ether is added to the solution, and the whole is shaken. All the coloring matter is dissolved in the ether, which will acquire different colorations according to the lakes introduced.

"*Lakes of Brazil wood.—First process.* Let us suppose that a madder lake is adulterated by the lakes of Pernambuco, Sapan, or Brazil wood, the coloring matter will be rendered soluble in ether by the process indicated above, and the ether will be colored a gold-yellow.

"*Venice lake, ball shape.—Second process.* A madder lake, adulterated by Venice lake, ball shape (one of the finest lakes of Brazil wood) will disengage ammonia if it be heated in a test-tube with a solution of potassa. Under the same treatment a pure madder lake does not produce ammonia.

"*Brazil lake.—Third process.* A madder lake, falsified with the lakes of Brazil wood, will be generally recognized by its effervescence with the acids, and its blue coloration by iodine. These reactions are due to the presence of chalk and starch, which are used for thickening the lakes made with Brazil wood.

"*Carmine lake.*—Another adulteration of madder lakes is that with the so-called carmine lakes, of an inferior quality. This fraud is easily detected.

"Water *is not colored* with madder lake, while it *is colored* with carmine lake. The coloration is immediate, and becomes more intense by heating. This aqueous solution of carmine lake becomes *violet* by soluble alkalies and gives a *violet* precipitate with lime-water, chloride of tin, sulphate of copper, acetate of lead, and sulphate of zinc.

"All that has been said about red and pink lakes may be applied to the *madder carmine.*

B. *Violet Lakes.*

"The violet madder lakes, after calcination, leave an ash of oxide of iron, which, being dissolved in hydrochloric acid, produce an abundant precipitate of Prussian blue by the addition of ferrocyanide of potassium.

"These lakes, under the action of hydrochloric acid, turn a dirty *orange-yellow* color.

"*Campeachy lakes.*—1. If adulterated with Campeachy lakes, the addition of hydrochloric acid will produce a *crimson-red* coloration. After calcination, the ash will be nankin yellow or white, whether the Campeachy lake is partly or entirely substituted for that of madder.

"2. After having extracted the coloring matter in the afore-mentioned manner, the ether is colored a gold yellow, and will give the Campeachy reaction, if that substance be present.

"*Alkanet.*—1. The madder lakes falsified by alkanet lakes are easily recognized. The lake is dissolved in *acetic acid*, and *bisulphide of carbon* is added, which, after shaking, is colored an intense violet red if alkanet be present. This reaction is characteristic of that substance.

"2. A madder lake adulterated by alkanet disengages violet fumes when heated. Moreover, such a lake is colored blue by alkalies, baryta, and lime.

"3. After solution of the adulterated lake in acetic acid, and separation of the coloring matter in ether, this is evaporated, and the residue is treated by alcohol, which dissolves the coloring principle of alkanet. This alcoholic solution gives a magnificent blue precipitate by the subacetate and the acetate of lead, if it contains anchusine.

"*Orchil.*—Orchil lake is dissolved in hydrochloric acid, which becomes red. Ether, shaken with this solution, does not dissolve a trace of coloring matter. The same reaction takes place with bisulphide of carbon.

"*Prussian blue.*—Prussian blue, added to a violet madder lake for the purpose of deepening the hue, is recognized by the addition of hydrochloric acid, which changes the violet of the lake to a green. Hypochlorites, and especially hypochlorous acid, turn the violet to a blue.

C. *Black Lakes.*

"By calcination, these lakes give an ash of oxide of iron. Hydrochloric acid changes them by degrees into a dirty orange. They turn a brown rusty color by the action of protochloride of tin.

"*Charcoal and lampblack.*—These lakes being of a fine black color, it is possible to falsify them with finely ground charcoal or lampblack. This fraud will be detected by boiling the sample with hydrochloric acid, which will dissolve the lake, and will leave the charcoal or lampblack as a residue.

"*Black Campeachy lakes.*—Black madder lakes may be mistaken for those of Campeachy. The latter will redden strongly by the action of hydrochloric acid and of the protochloride of tin. In the first case, the red portions will stain white paper a cherry-red color; and in the second case, a more or less violet red.

"*Lake with cochineal basis.*—In order to distinguish a black madder lake from one with cochineal basis, an addition of chloride of tin will turn the cochineal lake a cherry-red, and white paper will be stained. The madder lake presents no such reaction.

"*Black sumach lake, etc.*—While the black madder lakes are of a pure color, those manufactured from galls, sumach, and other astringent substances are olive-black. I do not believe that the latter can be mixed with the former, on account of the olive hue. Moreover, the adulteration must be considerable, in order to be profitable."

§ 20. *Violet, chocolate, brown, and red lakes of rhamnoxanthin and elder berries.*

When the boughs of several kinds of buckthorn (*Rhamnus frangula* and *Rhamnus catharticus*) are macerated for three or four days in bisulphide of carbon, according to Mr. T. L. Phipson, there is obtained a gold-yellow liquor, which, after evaporation at the ordinary temperature, leaves a yellow residuum. Alcohol dissolves the coloring principle of the residue, and leaves behind a peculiar fatty substance, which is of a brown color. Lastly, the alcoholic solution being evaporated to dryness, and its residue treated by ether, there are deposited, after spontaneous evaporation, crystals of a substance called rhamnoxanthin.

In order to obtain lakes, it is not necessary to extract the rhamnoxanthin in a state of purity, although it is the real coloring principle. The boughs of the buckthorn are steeped in a weak ammoniacal solution, which dissolves the coloring matter, and furnishes a purple-red liquor, which, after saturation of the ammonia by citric acid, and the addition of magnesia, produces a fine violet lake.

If protochloride of tin be added to the decoction in water of the boughs, and the liquor be precipitated by carbonate of ammonia, there is obtained a yellow-brown lake, which becomes of a chocolate color by the action of sulphuric acid.

With magnesia, chloride of tin, oxide of zinc, alumina, and oxide of lead, it is possible to form with rhamnoxanthin a number of brown, red, and yellow lakes, with very varied hues.

It is said that MM. Depouilly and Néron have obtained very handsome violet lakes, by treating elder berries (*Sambucus nigra* and *S. ebulus*) in the following manner: The berries are pressed in order to remove the seeds and the juice, and to collect the pellicles, which contain the greater part of the coloring matter. These pellicles are washed in cold water, and when they are quite clear, they are boiled in the same liquid, in order to obtain colored extracts, which may be more or less concentrated, and from which are prepared lakes for painting and for paper hangings.

§ 21. *Madder carmine.*

Madder carmine is an exceedingly bright red color, which is as durable as that of madder lake, and may be substituted for the same hues of cochineal. It was discovered by Mr. Bourgeois in 1816, and is still prepared by a secret process. Nevertheless, Mr. Lefort, in his *Chimie des Couleurs*, asserts that from his own researches, a very fine madder carmine may be obtained by the following process:—

"Avignon madder, of the best quality, is submitted to a kind of fermentation in a wet place. When it is supposed that the saccharine and bitter mucilaginous substances have been destroyed, and that the acid fermentation begins, the madder is disintegrated, and thrown into four times its weight of sulphuric acid, which has been reduced to 55° Bé. by an addition of water.

"The vessel in which the mixture is made should be of lead, and immersed in cold water, in order to avoid too great an elevation of temperature. The paste thus obtained is left to stand for about three hours. It is then diluted with 4 or 5 parts of water, and filtered upon a layer of broken glass, placed in a lead or glass funnel. The filtered liquor is received in a large volume of pure water, that is, free from lime, magnesia, or iron. The carmine is soon precipitated, and it is collected upon a paper filter, washed, and dried in the ordinary manner."

Madder carmine is employed especially for miniature and other artistic painting.

§ 22. *Lakes of red woods.*

The red woods of Brazil, Santa-Martha, Pernambuco, Sapan, and Lima contain a coloring matter, of a fine crimson-red color, which was by Mr. Chevreul called *Bresilin.* It may be precipitated by alumina with its natural color, but it changes to a bright pink when a certain proportion of protochloride of tin has been added to the solution.

These lakes are obtained by digesting the powdered woods in water containing $\frac{1}{20}$ of tartrate of potassa, and precipitating with a solution of alum. The precipitate is collected upon a filter, washed with cold water, and dried. Mr. Girardin says that the results are better, if the decoction of Pernambuco wood be precipitated by a solution of alum, in which chalk and starch have been put in suspension. The colored paste obtained is washed with cold water, drained, and formed into lumps, which are rendered firm by a small quantity of starch paste, and of rosin dissolved in essence of turpentine.

The *Venice lake, ball shape,* according to the same chemist, may be prepared by kneading a mixture of glue and gelatinous alumina in a concentrated decoction of Brazil wood, until the desired hue is obtained. The coloration is brightened by alum, and a violet reflex is imparted by soap.

The *flat lake of Italy* is a fine red color with but little durability. It is said to be a combination of alumina and lime with the coloring substances of Pernambuco or Santa-Martha wood.

Mr. G. C. Habich, who paid a great deal of attention to the manufacture of certain colors, has published, on the lakes of red woods, an article which is too important to be overlooked, and is as follows:—

"The precious coloring substances, furnished by the woods of Pernambuco, Lima, Santa-Martha, Sapan, etc., are all soluble in pure water. If these woods are treated with boiling water, their coloring matter is dissolved in combination with ammonia. Does ammonia exist in these dye woods, or is it a product of the destruction of vegetable albumen? I shall not try to answer this question at the present time. The presence of this ammonia, in the case of dyeing and preparing colors, is disadvantageous, because it facilitates the solution of certain brown substances, similar to humin, which tarnish the brightness of the colors. But as these humic substances are not soluble in water free from ammonia, we understand that they may be eliminated by a purification or a clarification of the colored decoctions. On that account, and in former times, it was usual for manufacturers of colors to let the decoctions stand for a long time. The small proportion of sugar held by them was, by fermentation, transformed into alcohol; the alcohol was, in its turn, transformed into acetic acid, which combined with the ammonia, and determined the precipitation of the brown matter. The red coloring principle, useful for the preparation of red lakes, remained therefore in solution with another deep yellow substance, and this solution was decanted from the deposit. This process, as we perceive, is very slow and takes several weeks. I have arrived at the same result by employing pure hydrochloric acid.

"The acid, diluted with an equal volume of water, is introduced in a stream, of the size of a straw, into the decoction of red wood, which is kept stirred all the while. The addition of acid is stopped when a filtered sample of the liquor has become yellow. The mixture is then stirred every half hour. The clarification is generally complete in a few days. The clear liquor is decanted, and the deposit is washed upon a filter. This purified decoction is then used for the preparation of red lake, which contains the coloring substance combined with alumina and oxide of tin. I shall not describe the manufacture of the aluminous lakes, known under the names of crimson lake, lake in ball, Vienna lake, etc., because the processes of preparation have been often described, and because the results are always good when the alumina salt employed is free from iron. I prefer giving some particulars in regard to the red Florentine lake, which is of a bright carmine-red, and is sought for by manufacturers of fancy and mottled papers.

"This fine color, which, unhappily, does not resist the action of light, is a combination of the coloring principle with the binoxide of tin. A combination may also take place with the protoxide of tin, but it is crimson, and without brightness. The manufacturer of colors should, therefore, pay great attention to the preparation of the tin solution, which should contain no protoxide or the corresponding chloride. The preparation of the proper solution will be certain, if we are guided by the following instructions:—

"The commercial tin salt is generally very impure, and it becomes absolutely necessary to prepare the tin solution on the spot. The purest English tin is melted, and transformed into irregular ribbons by the known process, that is, by letting it run from a height of about 2 metres, into water which is being moved in a circular direction. This tin, which presents a very extended surface, is put into two stoneware pots, one of which is filled with hydrochloric acid, free from iron, and marking from 20° to 25° Bé. After twenty-four hours, the acid is decanted into the second pot, and the metal remaining in the first pot is left exposed to the oxidizing action of atmospheric air. After twenty-four hours, the liquor of the second pot is poured into the first one.

"In order to transform this protochloride of tin into perchloride, the solution and an equal volume of the same hydrochloric acid are poured into a much larger vessel, holding six times as much, and immersed in a boiling water bath. If, then, nitric acid be added by small portions at a time, a tumultuous decomposition takes place, with production of red vapors. The reaction, which requires a few minutes, should be finished before a new quantity of nitric acid is added; indeed, rapid additions of acid may cause the liquor to run over. As a precaution against such an accident, the vessels and the water of the bath should be perfectly clean, so as to be able to recover (in a diluted state) any liquor which may run over.

"These additions of acid are continued as long as there is a strong effervescence. When the reaction shows signs of moderation, it becomes necessary to test with reagents the exact point of transformation, but before the tests are applied, the production of red vapors must have ceased.

"As a reagent, we may use a solution of hydrosulphuric acid, which should not produce any brown precipitate in a sample of the liquor. The precipitate may be a light yellow with hot liquors. Sulphurous acid should produce no precipitate whatever.

"When all the tin has been transformed into perchloride, the liquor is allowed to become clear, and we proceed to the precipitation of the coloring substance. The solution of tin is added to the colored liquor, which is kept stirred until a drop of perchloride of tin fails to produce a pink cloud in a sample of the liquor. The mixture is then stirred for half an hour.

"The proportion of perchloride of tin depends naturally upon that of the coloring matter. After having determined the amount by a preliminary trial, an equivalent proportion of perchloride of tin is poured into the colored liquor, and after a stirring of half an hour, another final test is applied in order to see whether the precipitation is complete.

"After decantation of the clear liquor, the color is washed with pure water. Should the water employed be calcareous, it should be rendered slightly acid with hydrochloric acid. This precaution is necessary, otherwise the washings may impair the brightness of the color.

"If the color is to be sold in paste, for instance, to manufacturers of fancy papers, there should be mixed with it none, or very little, of earthy substance. But if it be desired to produce a substantial color for theatrical painting, a certain proportion of finely ground plaster of Paris or alabaster, free from iron, is added. Many kinds of plaster of Paris contain a small proportion of carbonate of lime, which will impair the brightness of the color; but this inconvenience may be remedied by a washing with dilute hydrochloric acid."

A skilful manufacturing chemist has published in the *London Journal of Arts*, a new process for the manufacture of lakes from dye woods, which it is interesting to reproduce here, and is as follows:—

"It is possible with the salts of antimony, and preferably with the chloride, to precipitate the coloring matter of certain dyestuffs, such as Sapan wood, logwood, cochineal, quercitron bark, etc., and to obtain certain colors, known under the name of lakes, which have been prepared, up to the present time, with other metallic salts.

"In order to manufacture a red lake, the following substances are employed :—

"To 5 litres of chloride of antimony, marking 80° of the hydrometer of Twaddle, add 100 litres of a clear decoction of Sapan or Lima wood, marking 7° Twaddle. The whole is carefully stirred, and allowed to deposit for several hours, and is then filtered. The precipitate is washed twice, each time with 20 litres of water. After its draining, the lake is finished, and may be dried or sold in paste. With more diluted decoctions, the washings are not necessary.

"The proportions above indicated may vary according to the intensity of hue desired. With a greater proportion of chloride of antimony, the color will have a crimson hue; and if the proportion of the decoction of Sapan wood be increased, the hue will tend towards a scarlet.

"The same processes are followed for obtaining purple and violet lakes; but in this case, the Sapan wood is replaced by that of Campeachy (logwood). The following proportions give good results; 5 litres of chloride of antimony, marking 80° Twaddle, and 75 litres of a well-settled decoction of Campeachy, marking 6° Twaddle.

"In the preparation of yellow lakes, Sapan wood is replaced by quercitron bark.

"In the same manner it is possible to obtain lakes with all the dye drugs which form colored precipitates with the salts of antimony."

§ 23. *Vegetable violet.*

The vegetable violet is a lake which results from the combination of *hæmatoxylin*, the coloring principle of logwood, with alum and acetate of lead. It possesses a fine violet color, which, however, does not resist the action of light, and which, in the liquid state, should be preserved in tightly closed bottles of black glass.

It is prepared by dissolving 300 grammes of alum in 1 litre of hot water, and adding 250 grammes of crystallized acetate of lead, dissolved in a small quantity of water. Sulphate of lead is precipitated while a portion of the acetate remains in solution with the salt of alumina. On the other hand, a decoction of 600 grammes of logwood (Campeachy) is made in 5 litres of water, which, after cooling, is filtered through a cloth. To 100 parts of this decoction of logwood, 10 parts of the mixture of acetate of lead and salt of alumina are added, and afterwards a solution of gum Arabic, the proportion of which varies with the hue desired.

§ 24. *Carthamus red. Carthamin. Carthamic acid. Vegetable red. Spanish red. Red in plates. Portuguese red. Leaf red. Chinese rouge for the face.*

Carthamus red is the red coloring principle of the flosculous flowers of a plant (*Carthamus tinctorius*) called carthamus, safflower, German saffron, safranum, etc., which is very different from the oriental saffron, and which is cultivated in France and Germany.

This red coloring principle is by chemists called *carthamin* or *carthamic* acid; it is in the plant united with a yellow coloring substance, which is soluble in water, while carthamin is insoluble.

The color of carthamus used for rendering yellow the floors of dwellings, is a lake principally made of the yellow coloring principle. It is prepared by boiling carthamus in water holding a small quantity of alum, and adding curcuma (turmeric) for brightening the tone of the color. The yellow solution is employed for diluting the size.

The flowers, which have been thus deprived of the yellow principle by means of alum-water, or what is better, by water acidulated with acetic acid, contain only the red principle, and are ready for the extraction of the carthamus red. They are worked with their own weight of cold water holding from 15 to 16 per cent. of carbonate of soda. The liquor is filtered upon a cloth, and the same manipulation is repeated two or three times. The flowers are then thrown away. The liquors are collected in a wooden tub, filled with pieces of woollen or cotton cloth, which absorb the carthamin. These cloths are then well washed in pure water, and the color is removed by a solution holding 10 per cent. of carbonate of soda, which dissolves it. The color is again precipitated by a solution of pure citric acid. The flakes of precipitated carthamin are washed several times with cold water, then collected upon a filter, and dried in a dark place.

The dry carthamus red has a fine purple-red metallic lustre when it is in thin layers, but a large quantity of it appears green. Its hue may vary from a red to a pink, according to its quality and its state of comminution. This color, which is always very expensive, is employed by manufacturers of artificial flowers, for the imitation of flesh color in colored prints, by perfumers for the preparation of face powders, and also by dyers. It is to be regretted that it is not fast, and that it does not unite well with the liquid vehicles used in painting.

§ 25. *Indian red.*

Professor Dussauce has published in the *Technologiste*, June, 1861, an article upon a new red vegetable color, which we reproduce here.

"Painters," says he, "use but a small number of colors of organic origin, and those employed are generally in the state of lakes, that is, of combinations of a coloring principle with a metallic oxide or a salt. During my researches upon the coloring principles of vegetable origin, I have obtained from sandal wood (sanders) a substance which is nearly equal to carmine in beauty and brightness.

"This principle is durable, of a pure red, and melts at a temperature a little below 100° C. An increase of heat decomposes it. It is insoluble in water and the fixed oils, but very soluble in alcohol, ether, acetic acid, and the essential oils. Dry chlorine has no action upon it, but wet chlorine destroys it. Acids do not change it, except nitric and chromic acids, and those rich in oxygen. It stands sulphuretted hydrogen, light, and air well. Altogether it is a very durable vegetable color.

"Its preparation is very simple. Powdered red sandal wood is macerated with alcohol, and the alcoholic solution is treated with hydrated oxide of lead in excess. The resulting precipitate is collected upon a filter, washed with alcohol, and dried. It is then dissolved in acetic acid, and precipitated again by an addition of water in which it is insoluble. The acetate of lead remains in solution, and may be used for the preparation of the hydrated oxide of lead. The precipitate is again carefully washed with water, and dried at a low temperature.

"It would require too much space to give here all the researches by means of which I came to the conclusion that this color was pure santalin. Its price will not be over 10 francs per kilogramme, and I intend to prepare for dyers and printers a santalin compound which may be dissolved in water, a thing not hitherto discovered."

§ 26. *Cochineal carmine.*

Cochineal is a small insect of the genus *Hemipter*, and of the family of the gall insects, called by Linnæus *Coccus cacti.* This insect is originally from Mexico, but it is now successfully raised in the Canaries, in India, Spain, and Algeria. It feeds upon the nopal *Cactus coccinilifer*, L.

Cochineal, from the analysis made by Pelletier and Caventou, is composed of carmine or pure coloring principle; coccine or raw animal coloring material; stearin and olein; phosphate and carbonate of lime; chloride of potassium, phosphate of potassa, and potassa united with an organic substance.

In the trade cochineal is distinguished by the names of the countries from which it comes, Vera Cruz, Honduras, Canaries, and India; and each division is subdivided into types having each a gradation of hues. For instance, there is the black cochineal or zacatille, the marble or silvered cochineal, and sometimes the pinkish and wild cochineal. Each of the first three types is subdivided into fine, good, ordinary, commercial, and sometimes low commercial. Drug brokers base themselves upon the following examinations in establishing the grades of quality: 1. They examine the size, shape, and conformation of the insect, which is said to be hollow or filled according as the lower face is concave or level. If the edges are wrinkled, it is said to be curled. 2. The powder, from the greater or less beauty of its color, is a good index of its tinctorial value. 3. Lastly, the regularity of size of the insects, the presence or absence of foreign materials, the dust, dampness, etc., are also considered. A cochineal is said to be greasy when it sticks to the hands.

Several processes have been proposed for testing the value of cochineal. Thus Robiquet made a comparative test by decolorizing with chlorine, the decoction of the cochineal to be tried, and that of a standard article. Letellier based his method upon the difference of intensity in the coloration of two decoctions made with alum, one of the sample to be tested, and the other of a standard cochineal. Mr. Anthon has proposed to ascertain directly the proportion of carmine in a sample, by decolorizing the decoction with a solution of alum saturated with ammonia. Lastly, Mr. Oscar Kœchlin decolorizes a decoction of cochineal by chlorine, and checks the operation by another test with a solution of alum saturated with ammonia. None of these processes is, however, sufficiently certain and accurate.

The carmine of cochineal which is employed especially for water-color and miniature painting, for the manufacture of artificial flowers, etc., is the most magnificent red color we possess. Many processes have been tried for obtaining the carmine in a state of purity. Alum, cream tartar, solution of tin, caustic potassa, and the carbonate, nitrate, and binoxalate of that base, etc., have been employed. But this operation is always extremely delicate, and requires, to be successful, a great practice, many precautions, pure water, perfectly clean vessels, and an intelligent choice of raw material. We shall describe several of these processes.

A very great variety of carmines are found in the market, and their tone or hue is due to the process, or to more or less care taken in the preparation.

1. *Process of the old French Encyclopedia.*

"Take 20 grammes of cochineal, 2 grammes of *chuan** seeds, 70 grammes of the bark of *autour*,† and 1 gramme of Roman alum. Pulverize each of these substances separately in a clean mortar. Boil 2.33 litres of pure and clean water in a clean vessel, then add the chuan, and give it three boils. The liquor is constantly stirred with a wooden spatula. Filter the liquor through a white cloth into another clean vessel and boil. At the beginning of the ebullition, introduce the cochineal and give three boils, then the autour and another boil. Lastly, the alum is added, and the vessel is removed from the fire. Filter the liquor without pressing the cloth, and receive it into a clean porcelain vessel. After standing for seven or eight days, the clear liquor is removed, and the de-

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* *Chuan* is a yellowish-green seed of a plant coming from the East, and which Devaux recognized as the *anabasis tamariscifolia* of Linnæus.

† *Autour* is a light and spongy bark of a pale cinnamon color, which comes from the East. The tree which produces it is still unknown.

posit is allowed to dry in the sun or in a stove-room. The precipitate is then collected with a brush or a feather, and is a finely comminuted and colored carmine."

It should be remembered that carmine cannot be made in cold weather, because it does not settle, and forms a jelly which becomes decomposed.

The cochineal left in the cloth may be boiled again for a carmine of second quality. A small proportion of annotto is sometimes added to the chuan and autour.

2. *Ordinary Process.*

1 kilogramme of cochineal is dissolved, at a moderate temperature, in 20 litres of water holding 30 grammes of carbonate of potassa. After a few minutes of ebullition, the vessel is removed from the fire, and 60 grammes of powdered alum are dissolved in the liquor. The latter, which was of a deep red color, becomes carmine red, and is put aside until the cochineal has settled. The clear liquor is then decanted into another vessel, and is mixed with a solution of isinglass, passed through a sieve. The vessel is heated, and the carmine rises to the surface during the ebullition. The liquor is then removed from the fire, stirred, and allowed to settle for fifteen or twenty minutes. The deposit of carmine is drained upon a close linen cloth and dried. The remaining liquor is red, and is used for the manufacture of carmine lake.

3. *Chinese Process.*

The Chinese prepare the cochineal carmine by boiling 625 grammes of cochineal and 3 or 4 grammes of alum in 15 to 20 litres of pure river water. After a few minutes of ebullition, the vessel is removed from the fire, and the liquor is left to settle, and then filtered. The precipitation takes place by pouring in, drop by drop, a solution of tin made with 320 grammes of ordinary tin salt, 500 grammes of nitric acid, and 120 grammes of granulated Malacca tin. The precipitate of carmine is separated by decantation, and is received upon a filter, and dried in a dark place.

4. *German Process.*

The cochineal is boiled in alum-water. After boiling for some time, more powdered alum is added, and the boiling continued. The liquor is then removed from the fire, decanted, filtered, and allowed to remain in porcelain vessels, in which the carmine precipitates slowly. After three days, the deposit is collected and dried. The mother liquors are preserved, and give another quantity of carmine, which is inferior to the first.

5. *Process by Cream Tartar.*

Put cream tartar (bitartrate of potassa) in the water where cochineal is being boiled, and after boiling for some time add powdered alum. After a short boil, remove from the fire, filter, and the carmine becomes deposited.

6. *Process with Wool, and Formation of a Lake.*

Take 250 grammes of cochineal, 1 kilogramme of alum, 250 grammes of cream tartar, and 250 grammes of wheat bran. All these substances are ground, and thrown into 20 litres of boiling water; 250 grammes of white wool are then put in, which absorbs the carmine. The wool is removed, drained, and immersed, still wet, into a solution of caustic potassa which takes up the coloring matter. The latter is precipitated by a solution of alum.

7. *Wood Process.*

Mr. Wood has recently proposed another mode of preparation, which appears to possess real advantages. The carmine is of a magnificent color, and is said not to change by time or by exposure to the air.

250 grammes of pure carbonate of soda, and 225 grammes of citric acid, are dissolved in 30 litres of water. When the whole is boiling, 680 grammes of powdered cochineal are aided, and the ebullition is continued for 1 or 1.5 hour. The liquor is filtered and allowed to cool off; and when it has become clear, it is boiled again for 5 minutes with 250 grammes of alum. After a second filtration, it is allowed to stand for two or three days. The clear liquor is then carefully decanted from the deposit, which is washed with cold distilled water, and dried at a low temperature in a stove-room. The impalpable powder thus produced is, if desired, mixed with water rendered alkaline by ammonia, and mucilaginous by gum Arabic. By evaporation, the product may be moulded into small blocks.

This carmine may acquire a peculiar red lustre, by being mixed with 250 grammes of alum and a few decigrammes of a tin salt; for instance, the sulphate, the nitrate of protoxide, or the chloride of this metal.

8. *Grelley Process.*

Mr. Grelley has proposed a method of treating cochineal, which allows of the almost entire solution of its coloring principle, and of the preparation of very handsome red lakes.

First, the ground cochineal is digested for four or five hours in water slightly acidulated with hydrochloric or sulphuric acid. Second, the acid is saturated with an excess of ammonia, and the latter is left to act for ten to twelve hours. Third, the solution is decanted, and the deposit is pressed, so as to lose no liquor. Fourth, the excess of ammonia is saturated with one of the above indicated acids, which is diluted with four or five times its weight of water. Fifth, the useless precipitate formed by the last treatment, is separated by means of flannel filters. These solutions give immediately a fine ponceau red lake, when they are precipitated by a mixture (half and half) of the two chlorides of tin, mixed with a small quantity of water.

The aluminous lakes are prepared by treating these solutions, first, by alum, and then by a caustic or carbonated alkali.

This process is equally good for fresh cochineal, and for that which has been already boiled.

§ 27. *Carmine lake. Paris lake. Vienna lake.*

Carmine lake is prepared with the mother liquors from which the pure carmine has been extracted, and which still contain a great deal of color. A solution of alum is added, or a certain proportion of recently precipitated alumina is stirred in, and the color is brightened with a small quantity of protochloride of tin. The precipitate is washed, moulded into troches, and dried.

The lake is the finer as less alum or alumina is employed; and it is quite customary, for the inferior qualities, to give them more body by an addition of starch.

The finest kinds of lakes are prepared from fresh cochineal, which has not been previously boiled. 20 parts of powdered cochineal are boiled in 400 parts of water, holding in solution 10 parts of cream tartar. The liquor is filtered, and is mixed with a solution of 300 parts of alum, and a very small quantity of protochloride of tin. The precipitate, which deposits after a little while, is very bright, and is collected. A solution of carbonate of potassa is then slowly added to the liquor, which is kept stirred all the time. The new precipitate formed is thrown upon a filter, washed, and dried.

In this manner, a first and very handsome lake is obtained, and those which follow are made more or less rich in color, by adding more or less of the solution of alkaline carbonate.

§ 28. *Ammoniacal cochineal.*

Caustic and concentrated ammonia dissolves the carmine of cochineal, and, at the same time, increases the brightness of the color. This property has been made use of for preparing what is called ammoniacal cochineal, and which is sold in paste or in cakes. One part of carmine is dissolved in 6 parts of commercial aqua ammonia, kept in a well stoppered glass bottle. After several days of exposure to the sun, and with frequent shakings, the ammonia has dissolved the carmine. The liquor is then filtered, and precipitated with acid and alcohol. The resulting carmine is washed with dilute alcohol and dried.

§ 29. *Red and violets from archil.*

A great many researches and articles on archil have been published; but we do not recognize in them the exactness required by modern chemistry. We shall therefore confine ourselves to a recent article by M. H. Gaultier de Claubry, where the preparation of this coloring substance is better understood and explained.

The remarkable discovery of *orcin* by Robiquet demonstrated the presence, in certain lichens, of a colorless substance, which, under the combined action of air and ammonia, is transformed into a fine violet color. So is indigo, which is colorless in the plant, but becomes blue by contact with the air. Several natural products extracted from lichens, lecanoric acid for instance, result, under certain circumstances, in orcin, which may be a derived product. These lichens are treated for obtaining archil, and this color is always produced under the combined action of air, ammonia, and water. Urine has, for a long time, been used for that purpose, and Cocq proposed to substitute for it ammonia, which has already been employed in Germany, as seen by a memoir of Hermbstaedt (*Magazin für Farber*, I. 290). There are several reagents which will extract from lichens the substances which are transformed into orcin; for instance, water, alcohol, and alkaline solutions. Notwithstanding the great number of researches published on the subject, it is impossible to decide with certainty upon the state in which these substances exist in the plants. Moreover, the latter present great differences in their nature and in their origin.

The product known under the name of archil is not a single colored substance, but a compound of several. Although similar in color, they vary in their resistance to the action of certain agents, and, according to their relative proportions, they give to the compound peculiar qualities for dyeing.

The archil-lichens give at most 10 to 12 per cent. of available products. If these be separated from the mass of the plant, and then submitted alone to the influence of the air and of the ammonia, the tinctorial product is obtained under conditions much more favorable than by the ordinary processes.

During his researches upon these lichens, Stenhouse employed lime instead of ammonia, as Heeren did, for extracting the color producing substances. This process may be applied; but, according to the mode of operation, the results may be entirely at variance. It is sufficient, says Stenhouse, to cut the lichens and to macerate them in a milk of lime, and then to saturate the solution by hydrochloric or acetic acid. All the available coloring product will thus be obtained, and after a further treatment by air and ammonia, it will be transformed into archil. The promised result is indeed obtained, but only under given circumstances, that is, if the maceration be very short, as we shall prove further on. The word maceration, unless accompanied by the length of time the substance and the liquid should be in contact, is entirely too uncertain, as upon it depends the success or failure of the operation. A maceration is generally a long operation, lasting one, two, or several dozens of hours, and it is therefore necessary to determine accurately all of the conditions necessary to arrive at a given result.

Whatever be the time of contact of the lime with the coloring principles, the latter will be dissolved, and one of two cases will be presented: Either an acid will precipitate the whole coloring matter under a small volume, which will then be transformed into archil by treatment with ammonia; or the acid will produce no precipitate, and the coloring matter will remain entirely in solution. In the latter case, evidently all of the advantages of the treatment by lime disappear. The following experiments demonstrate these results completely. 100 grammes of Madagascar lichens were immersed in 600 grammes of a milk of lime, holding 30 grammes of lime. After the periods of time indicated, the insoluble parts were separated upon a hair sieve, and washed. The liquors were treated by hydrochloric acid in excess. Each precipitate was collected upon a cloth, washed, and dried. The liquors were neutralized by ammonia, and concentrated by evaporation; afterwards an excess of ammonia was added, and they were kept, a part of the time, at the ordinary temperature, and the remainder in a store-room heated at from 50° to 60° C.

Length of maceration.	Precipitate.		Liquors.
15 minutes.	12 grammes, furnishing a great deal of archil.		Scarcely any coloration.
1 hour.	12.5 grammes, furnishing a great deal of archil.		Distinct archil coloration.
2 hours.	9.3 grammes,	less archil.	A bright color.
3 "	8 "	still less.	A brighter color.
4 "	4 "	less again.	A still brighter color.
6 "	2.7 "	less.	A richer color.
8 "	2 "	very little.	Fine archil.
12 "	1.1 "	scarcely any.	" "
24 "	0.5 "	scarcely any coloration.	" "
48 "	0.5 "		" "

By repeating the experiment with double the proportion of lime the precipitate was smaller from the second hour, while, at the same time, the liquor contained a great deal of archil.

These numbers cannot be given as absolute, but they demonstrate in the most positive manner that, by submitting lichens to the action of a milk of lime, it is possible, in accordance with the mode of operation, to obtain the coloring material by precipitation, or to leave it entirely in solution.

Water alone produces a similar effect, but a great deal more slowly. A protracted contact will render the coloring products soluble. On the other hand, a very short contact will cause a separation.

If, instead of operating at the ordinary temperature, the lime liquor be made to boil for three or four minutes only, the addition of an acid separates a brown material, the color of which deepens by contact with ammonia, but which furnishes not a trace of archil either at the ordinary temperature or with an increase of heat.

If, instead of lime, various soluble salts be substituted, such as the phosphates of soda, potassa, or ammonia, borax, the carbonates of potassa or soda, etc., the transformation of the coloring substances is very rapid, and an ebullition of a few minutes is sufficient to prevent the formation of any precipitate by saturation with an acid.

Powerful alkalies, such as potassa, soda, baryta, and strontia, cause the tranformation more quickly than lime.

As I have previously stated, the product known under the name of archil contains several coloring principles, which unequally resist the action of various agents. That obtained at the temperature of 60° C.

contains the greater proportion of the more durable principles. On the other hand, the archil prepared at the ordinary temperature contains a greater or less proportion of alterable elements.

For some time past, either in France or in other countries, the manufacture has been conducted with the aid of heat, and the operation is more rapid and economical.

§ 30. *Perchloride of chromium.*

This product, according to Mr. Wöhler, forms a mass of red, bright, and micaceous laminæ, which may be ground like talc between the fingers. It will be used as a coloring substance, especially for paper hangings, when it becomes possible to manufacture it at a reasonable price. The following is the mode of preparation:—

Small balls, made of a mixture of oxide of chromium, charcoal, and flour paste, are brought to a high temperature in a covered crucible, and then put into an apparatus composed of a large crucible, standing upon the grate of an air furnace, and which connects with a chlorine generator by means of a porcelain tube, which is luted on to a hole made in its bottom, and which passes through the grate. The upper part of the tube does not project much inside of the large crucible, and is loosely covered with a small inverted crucible, so as to prevent the balls from falling in. A second large crucible is inverted and luted to the first, and has also a small hole in its bottom for the escape of the gases.

As soon as the apparatus is filled with gaseous chlorine, the lower crucible is raised to an intense heat, and the fire is so conducted that the sublimed perchloride of chromium condenses in the upper crucible, the temperature of which is not above a dark red heat. As the perchloride of chromium, heated in contact with the air, is decomposed, it is necessary to continue the passage of chlorine during the cooling of the apparatus. The operation should be conducted in the open air, or under a chimney with a good draft. The perchloride is then washed with water, to remove the chloride of aluminium resulting from the clay of the crucible. If the flow of chlorine has been weak, the product will contain a certain quantity of simple chloride, which, during the washings, causes the solution of a portion of the perchloride, which is thus lost.

§ 31. *Chrome red.*

We have already described the manufacture of this fine product, when speaking of the preparation of chrome yellow, by the process of Mr. Habich.

SECTION V.

BROWN AND BLACK COLORS.

I. BROWNS.

§ 1. *Mars browns.*

While examining the preparation of ochres, we have seen that, by calcining a Mars yellow at various temperatures, and under peculiar conditions, this substance passes through a series of colors and hues, among which there is a brown of sesquioxide of iron which is very durable, but somewhat expensive.

We shall here indicate a process due to Mr. Salvetat, by which it is possible to obtain a brown, and also a red ochre of great brightness.

A solution is made in hydrochloric acid, of 280 grammes of metallic iron, and 330 grammes of zinc. The whole is afterwards precipitated by the carbonate of soda, and the precipitate is carefully washed, in order to remove all the chloride of sodium or carbonate of soda. The deposit, which is green at the beginning, becomes brown; and, when all greenish hue has disappeared, it is drained upon sheets of filtering paper spread upon cloths. Lastly, the dried product is brought to the desired hue by calcination upon clay dishes.

The zinc and iron may be replaced by the sulphates of these metals, provided their composition be taken into account.

The tone or hue of the pigment is modified by mixing 1, 2, 3, . . . equivalent weights of zinc, with 2, 4, 6, . . . equivalents of iron. The addition of nickel, cobalt, or manganese produces darker hues, resembling wood, sepia, etc.

§ 2. *Iron minium.*

MM. Bouchard and Clavel have made many experiments for doing away with red lead in painting and in the manufacture of mastics, and they have taken as a substitute a Burgundy ochre.

Since then, they have taken out a patent for a new product which they call *ferrugine alumineuse*, which replaces red lead very advantageously as regards economy, and presents none of the inconveniences of the lead product.

A new color, preventive of rust, and which may enter into the composition of cements, has recently been manufactured. It is iron minium, which seems intended to take the place of red lead in iron and wood painting. We borrow from the *Génie Industriel* the following paragraphs:—

“The new product possesses all the qualities of red lead, without any of its inconveniences. It is of a fine brown color, constant in price, and mixes perfectly well with linseed oil. Under equal volumes, it covers more than red lead, and is a better protection against oxidization.

“Iron minium is a very pure substance, into the composition of which no acid enters, nor any other combination hurtful to the painted articles. In fact, according to Mr. Loppens, professor at the Industrial School of Ghent, it is a composition which cannot be altered by any of the causes generally acting upon red lead, and which may replace the latter in all its uses.

“Three different analyses of iron minium gave—

I.	Water	1.3
	Clay	25.7
	Red lead*	3.2
	Carbonate of lime	0.6
	Peroxide of iron	67.7
	Loss	1.5
		100.0
II.	Silica	0.105
	Alumina	0.035
	Peroxide of iron	0.820
	Lime	0.020
	Water	0.010
	Magnesia	0.010
		1.000
III.	Peroxide of iron	68.95
	Aluminous earth (clay)	1.48
	Burnt clay	29.57
		100.00

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* This red lead comes from the litharge employed as a dryer.

"After experiments on painting, made under the direction of Dutch engineers, in comparison with red lead, the comparative weights were—

Red lead	1.47
Iron minium	3.13

"And the specific gravities, by hydrostatic process at 22° C.—

Iron minium	3.74
Red lead	8.24

"The analyses prove the absence of any kind of acid, which, even in the smallest proportion, alters the colors, especially when it is sulphuric or hydrochloric acid.

"A comparison of these analyses with those made of *Oriental brown*, *Burgundy red*, *caput mortum*, or *colcothar*, shows the great superiority of iron minium.

"Colcothar always retains a trace of sulphuric acid. Indeed, it is the residue of the manufacture of the Nordhausen sulphuric acid, which is prepared by the distillation of sulphate of iron. Iron, coated with this pigment, is rusted, instead of being preserved.

"*Employment of iron minium.*—We know that red lead is simply mixed with raw or boiled linseed oil, and that the mixture dries so rapidly that it should be prepared only a short time before its use. Moreover, its manipulation is unhealthy, and may occasion lead colic, the same as white lead.

"The preparation of iron minium for painting is quite like that of red lead, that is, it is simply mixed with raw or boiled linseed oil. If thin coats are desired, the mixture is ground, and a little litharge dryer is added, preferably to essence of turpentine which, as a general rule, does not improve colors.

"In painting the hulls of ships, red lead is mixed with a certain proportion of bisulphate of mercury, which is a virulent poison, and is intended to destroy molluscs and wood boring insects. This poison may be incorporated with iron minium, which is not thereby altered.

"Mixed with one-third of white lead, iron minium forms an excellent mastic, similar to that made with red lead, and which is much cheaper, and becomes very hard after drying for some time.

"As the paint made with iron minium resists a strong heat, it may be advantageously employed for painting the interiors of boilers, and preserving them from incrustation.

"Mixed in certain proportions with coal tar, iron minium forms a very firm coat, which penetrates the pores of the wood and hardens it considerably.

"The brown color of iron minium is not altered by the sulphides, while red lead is, and remains a long time in its natural state. It will, therefore, be found advantageous and economical to use this paint for the hulls of vessels in ports where the filth of the city is poured into the docks."

§ 3. *Van Dyke brown.*

Van Dyke brown is also a color derived from iron, and is very durable.

It is prepared by the calcination of certain yellow ochres found in the south of France. The resulting frit is sold in lumps, in grains, or as an impalpable powder. Ochres, as we know, hold alumina and sand, which combine with the oxide of iron at a high temperature.

A Van Dyke brown is also manufactured by calcining sulphate of iron several times. The proper color is arrived at by practice. We understand that this last brown, which is entirely an oxide of iron, and of a purer color than the preceding, is more expensive. It is often adulterated with the brown frit, and the fraud is detected by means of concentrated and hot acids, which easily dissolve the pure oxide of iron, and with difficulty the ochre brown.

By mixing Van Dyke brown with variable proportions of red ochre and binoxide of manganese, very durable browns are obtained, which do not require dryers when they are used hot.

Other durable browns may also be prepared by mixing this pigment with lamp or ivory black.

§ 4. *Manganese brown.*

Mr. J. Lefort, in his *Chimie des Couleurs*, states that the analyses of old Roman paintings show that the oxide of manganese was employed as a brown pigment. This chemist has, therefore, made a few experiments by which he has ascertained that the binoxide of manganese ground in oil, gives a very handsome and durable paint. He proposes to manufacture this color as follows:—

"The protochloride of manganese resulting from the manufacture of chlorine, or the protosulphate obtained by the calcination of the protoxide of manganese with sulphate of iron, is dissolved in water at the temperature of 30° to 40° C. Then a solution of hypochlorite of soda (Labarraque's liquor), or one of hypochlorite of potassa (Javelle's water), holding a certain quantity of carbonate of soda, is added until the precipitate formed does not change color. When the oxidization is complete, the liquors are decanted and the precipitate is washed first with water holding $\frac{1}{50}$ of sulphuric acid, and then with pure water until the rinsings are tasteless. The binoxide of manganese, after being dried in a stove-room, is an impalpable and dark-brown powder, which covers well and is entirely innocuous."

§ 5. *Brown of manganate of lead.*

Take 1 part of oxide of manganese, 1 of oxide of lead, and 1 part of sulphate of ammonia, and mix the whole with peat, so as to form a paste which is dried and burned. The resulting pearl-gray compound is then mixed with 1 part of nitrate of lead and 1 part of sulphate of iron, and the product (after calcination ?) is said to be a fine sienna earth.

§ 6. *Prussian brown.*

Mr. Bouvier has indicated a process for preparing this brown, which was discovered by the painter Tœffer.

"Heat an iron ladle upon a brisk fire until it becomes red, and then throw into it pieces of Prussian blue of the size of a filbert. Each piece will soon split, scale off, and become red. Then remove the ladle from the fire and let it cool. A longer heating will destroy the desired color. When the pieces are broken, there are seen black parts mixed with others of a yellowish-brown color, which is the proof of a good preparation. Grind the whole together, and there will be produced a brown resembling bistre or a very clear asphaltum."

This process would be improved by calcining in a closed vessel. The product would be more homogeneous, and the temperature more easily regulated for a given tone of color. This pigment is very durable and covers well.

§ 7. *Red-brown.*

We have described the preparation of this color in Section IV., § 5, and we have seen that it is a mixture of oxide of iron and litharge, or red lead, which is fused in a crucible.

§ 8. *Gilt-brown.*

This brown is a binoxide of lead, and is prepared as follows :—

Orange mineral, litharge or red lead, is very finely powdered, and heated in a vessel with Javelle water or chloride of sodium (hypochlorite of soda ?), added by small quantities at a time. The material becomes gradually brown, and when the desired tone of color has been obtained, it is washed and dried.

Mr. Lefort asserts that the product is of a finer quality when white lead is employed.

§ 9. *Chicory-brown.*

When certain vegetable substances are burned in closed vessels, the root of chicory for instance, there is obtained a fine powder which, after boiling in water, gives a colored solution. If the latter be evaporated to dryness, the residue is a brown substance, soluble in water, and which is employed in water-color painting. The color is rich, but not durable.

§ 10. *Ulmin-brown.*

Duménil recommends as a color for miniature painting, the brown deposit formed by the action of caustic potassa upon alcohol. Fused caustic potassa, coarsely broken, is digested with twice its weight of alcohol, and then filtered through a cloth.

The liquor is heated for a few hours, becomes dark-brown, and deposits a dull-looking powder, which is collected upon a filter and washed with water acidulated by hydrochloric acid.

By melting in a copper vessel, three parts of sugar with one of potassa, until the mixture becomes a dark brown, and then dissolving in water, filtering, and precipitating with an excess of hydrochloric acid, there is produced a brown color, which is, however, inferior to the preceding one.

This color may also be obtained by treating peat, cotton, lignites, etc., by alkalies; starch, flour, etc., by concentrated acids; or wood-soot, bistre, etc., by caustic potassa.

Ulmin-brown is a fine color, which mixes well with other pigments, and flows well under the brush.

§ 11. *Bistre.*

This water color is prepared from the soot which accumulates in the flues of fireplaces in which wood is burned. Its preparation for becoming a pigment is as follows:—

The brightest and darkest fragments of soot, resulting from the combustion of beech-wood, are powdered and passed through a silk sieve. The powder is stirred in hot water for twenty-four hours, and again in another water. All the liquors are collected and allowed to settle. The precipitate is then mixed with gum-water, and evaporated in a stove-room to the consistency of a solid extract.

§ 12. *Bitumens or Asphaltum.*

Such are the names given to various liquid or solid substances, which melt at a moderate temperature, and have a more or less pungent and peculiar smell. They are very combustible, and leave a small charred residue, which is very light and easily reduced to ashes. The *bitumen naphtha* is abundant in Persia, upon the shores of the Caspian Sea, near Bakou, etc. It oozes constantly from the soil, and is accompanied by hydrocarbon gases, which are burned by the inhabitants for various purposes. This bitumen is also found in Calabria, in Sicily, in America, etc.

Bitumen of Judea or *Asphaltum.*—This is the kind most generally used in painting, and it is found on the surface of the Dead Sea. It has also been found, under ground, in America, China, the island of Trinidad, France, Germany, Seyssel, Ussel, Dax, etc., and in the Carpathian Mountains. Asphaltum is black or brown, solid, hard, fusible, and breaking with a smooth fracture. When pure, it is insoluble in alcohol, very combustible, and leaves a residue amounting sometimes to 15 per cent. It was employed by the Egyptians for embalming their dead.

Bitumen or *Retin asphaltum.*—This substance is of a light-brown color, with a resinous fracture, very fusible, and partly soluble in alcohol.

Melted bitumen becomes very brown and transparent. But as it destroys the drying quality of oils, it should be dissolved in essence of turpentine. This solution, which can be made in the cold or with very little heat, is so thick, that in order to paint with it, it requires to be mixed with the emplastic oil of the Italians and with a mastic varnish.

A very drying bitumen may be prepared by the following process:—

Venice turpentine	15 parts.
Gum-lac	60 "
Asphaltum	90 "
Drying linseed oil	240 "
White wax	30 "

The gum lac is dissolved in the turpentine by portions at a time, and no more is added until the previous addition is melted. The asphaltum is then treated in the same manner. While this operation is going on, the linseed oil is heated nearly to the boiling point, and afterwards mixed by degrees with the melted asphaltum. Lastly, the wax is added before cooling. The whole is poured upon a stone slab, and worked with the muller or the knife.

Since it has become possible to employ the pure bitumen, and to render it drying and easily ground, Mummy and Van Dyke browns are much less employed, because these latter pigments are often adulterated with other coloring substances.

Bitumen or asphaltum stands the action of light quite well; but the tone of its color, its durability, and its transparency vary with the nature of the bitumens and the mode of preparing them. The bitumens generally found in the trade are those of Judea, Grenoble, and Strasbourg. When pure, they burn and leave very little ashes, or none at all.

§ 13. *Sepia.*

Sepia is furnished by a marine cephalopod, the cuttle-fish (*Sepia officinalis*), which is very common on our shores. This color is extracted from a pocket filled with a brown liquor, which the fish emits in order to obscure the transparency of water when it is pursued by its enemies. As soon as it has been caught, this pocket is removed and dried in the sun. It is then powdered, ground with a concentrated solution of carbonate of potassa, and boiled for some time. The solution is filtered, saturated with an acid, and left to settle. The precipitate is washed first by decantation, and afterwards upon a filter, and then dried. This pigment forms an impalpable powder of a dark-brown color, insoluble in water or alcohol, and is very fine and durable.

§ 14. *Umber.*

This earth appears to be a hydrated silicate of iron and manganese, which is found native, and was formerly imported from the Roman province of Umbria. It now comes from the island of Cyprus. The natural article is in the state of brown lumps, adhering to the tongue, staining the flesh, and falling to powder in water. The impurities are removed by washing, and the floated article, after settling, forms a light-brown powder, which is employed raw or burnt.

Powdered umber, or that which has been calcined too much, reddens or blackens by the dehydration of the iron or the superoxidization of the manganese. It is rarely employed alone, and it mingles well with other colors or with slaked lime.

§ 15. *Sienna earth.*

This is an earthy substance, exported from Sienna, in Tuscany, and which owes its color to a hydrated oxide of iron. It is used raw or burnt.

Raw sienna is a dark-yellow on the exterior, and a light-yellow inside; its powder is greenish-yellow. Burnt sienna is either a light or dark-red when in lumps, but its powder is of a dark-red color.

§ 16. *Cologne and Cassel earths.*

Cologne earth is a brown earthy substance, which takes fire easily, and burns without flame or smoke like decayed wood. It produces white or red ashes, and presents all the characteristics of organic materials. It is found in the neighborhood of Cologne, especially at Brühl and Liblar, where it forms considerable deposits, as much as 12 metres in thickness, and extending over several kilometres.

This earth is smooth to the touch, crumbles to a fine powder, is as light as water, and of a brown-black color. The impurities are separated by washings, and the pigment is moulded into large troches, which, being ground in water or oil, give a very durable and fine brown color.

§ 17. *Puce with chromate of manganese.*

According to Mr. Persoz, the calcined chromate of manganese gives a handsome puce (flea) color, which may be used for oil and porcelain painting, and for calico printing with albumen.

II. BLACKS.

A. MINERAL BLACKS.

§ 1. *Schist or shale black.*

This black is obtained by the carbonization of bituminous schists in closed vessels, but all kinds are not equally good for this manufacture, and the light schists are generally preferred, the Scotch *Bog-head* for instance.

In the arts the latter schist is calcined in large cast-iron retorts, and there are obtained essential oils for lighting, certain gases, and a carbonaceous residue which has received the name of schist black.

By a slow distillation and a moderate heat, boghead furnishes from 35 to 40 per cent. of crude oil, weighing on an average 850 grammes per litre, that is to say, a sp. gr. = 0.850. The carbonaceous residue amounts to about one-half of the distilled schist, and is directly removed from the retorts into closed iron vessels, where it cools off without the contact of the air. It then forms light and porous lumps, which are easily ground.

This charred mass from bog-head contains from 30 to 35 per cent. of pure carbon, and from 70 to 65 per cent. of alumina mixed with a small proportion of silica, magnesia, lime, and sulphide of iron.

This material has been but recently used for painting. It combines readily with drying oils, and gives an intense and handsome black, which is at the same time very economical.

§ 2. *Bituminous coal black.*

Mr. P. T. Lavalleye has proposed to manufacture a black color with bituminous coal in this manner:—

"Two pairs of ordinary millstones are necessary, in which coal is substituted for wheat.

"Small coal (slack) is to be preferred, since it is cheaper than the large, and saves the expense of breakage. If, however, there are too large lumps, they should be broken with a hammer.

"After the coal has passed through the first pair of stones it goes through the second, the stones of which are one-third nearer each other than the first set.

"The powdered pigment is then ground again as usual with essence of turpentine, or linseed oil, or varnish, according to the use it is intended for. It is suitable for all kinds of oil painting, for houses, carriages, etc. It is also employed in distemper painting with size and milk."

§ 3. *Black of chromate of copper.*

Mr. Persoz has demonstrated that the basic chromate of copper contains three equivalents of oxide of copper, and that by calcination it loses a portion of its oxygen, and is transformed into an oxide of copper soluble in hydrochloric acid, and into a compound insoluble in that acid.

The calcination should take place in contact with the air, and not in a closed crucible, because, in the latter case, the resulting salt is different and contains the copper in the protoxide state. This second compound resembles galena, while the first is an amorphous black powder.

The pigment, obtained by calcining in the air the basic chromate of copper, may also be produced by the calcination of a mixture, in fixed proportions, of bichromate of potassa and nitrate of copper. It is remarkable for the intensity of its black amorphous color, its comminution, and its unalterability. It may be employed in oil colors, and probably also, in porcelain painting, and calico printing with albumen.

§ 4. *Ebony black.*

It is said that a fine ebony black color may be obtained by burning nitrate of copper with peat.

B. VEGETABLE BLACKS.

§ 5. *Peach-stone black.*

This black is prepared by calcining in closed vessels, the stones of peaches, apricots, and other fruits. The calcined stones are broken in a cast-iron mortar, and the powder, after having passed through a silk sieve, is ground in water. The color is handsome, but has a reddish tinge. Ground with oil and white lead, the color called in England *old gray* is obtained.

§ 6. *Fusain* (*spindle tree, prickle wood*) *black.*

This black is the result of the calcination of the prickle wood. The *dry* wood is divided into small rods, which are placed in a crucible of cast-iron or of thick sheet-iron. A layer of sand, from 8 to 10 centrimetres thick, is placed between the wood and the crucible cover, which has an opening for the escape of the gases. The crucible is then brought to and maintained at a red heat for two hours. After cooling, the rods of charcoal are removed, and cut in the shape of pencils.

It has been remarked that the young branches give a lighter and a better charcoal than the old wood.

§ 7. *Grape-vine black.*

This is the product of the carbonization in closed vessels, of the clippings of grape-vines at the pruning time. The black is very intense and light, and is ground by the ordinary process.

§ 8. *Cork black.*

This black, also called Spanish black, is prepared by calcining in closed vessels the waste of cork cuttings. It is very fine, and, combined with other pigments, it produces very handsome hues.

§ 9. *German black.*

This black is very much employed for copperplate printing, and is obtained by the calcination in closed vessels, of a mixture of grape stalks, dried wine lees, peach-stones, and bone waste. The proportions of these various substances are not very constant, and a very fine black may be produced from the following proportions: 3 parts of unboiled bones, 7 of dry stalks, 5 of dry wine lees, and 6½ of peach-stones from the residue of the distillery. If the peach-stones have not been distilled, 5 parts are sufficient.

After cooling, the charcoal is removed from the crucible, and powdered in a mortar. The powder is passed through a silk sieve, and then ground in water. The paste, brought to the proper consistency, is moulded into lumps, which are dried in a stove-room, and constitute a German black of the first quality.

§ 10. *Frankfort black.*

Frankfort black is prepared by burning wine lees in closed vessels, powdering and grinding the charcoal in water, and then moulding it into cakes. The *charcoal black* for printing is prepared in the same manner. The grinding is effected between stones kept in a kind of tub, in the bottom of which there is an opening for removing the ground product. In works arranged for the purpose, the motive power, horse or steam, is generally in the centre, and drives on one side the stamps for pulverizing, and on the other the mills for grinding. Tubs raised somewhat above the ground are placed along the walls, and receive the ground black, which is allowed to settle. After the decantation of the liquor above, the black is drained in baskets lined with cloths, and then moulded and dried. The moulds are 8 centimetres in height and 10 in diameter, and are formed each of a thin wooden ring. Several such moulds are placed upon a board before being filled with the black paste.

These various kinds of black are employed for painting, for copperplate printing, etc. The sticks of fusain are used for sketching.

§ 11. *Lampblack.*

The manufacture of lampblack is quite an important branch of trade in certain localities. This black is obtained by the incomplete combustion of substances very rich in carbon, and which burn with a fuliginous flame. This combustion produces a black dust, exceedingly light, which is known in the arts under the name of lampblack.

The substances generally employed are resins, tar, heavy oils from tar and schists, and vegetable oils. The latter give the finest and purest black, but its price is higher.

There are in the trade three principal kinds of lampblack:—

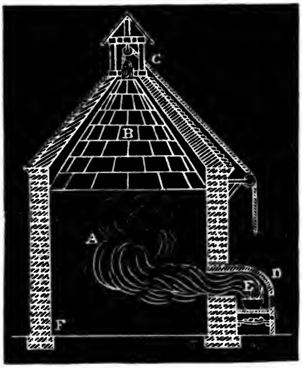
1. The resin black;
2. The tar black;
3. The oil or lampblack.

We shall describe the process for manufacturing each, in the above order.

First Process.—Resin Black.

As is indicated by its name, this black is obtained by the combustion of resins. The apparatus is composed of a cylindrical building A (Fig. 59), lined inside with hanging cloths, upon which the black condenses. This building is covered with a conical roof, supporting a movable sheet-iron cone B, which is perforated at its summit in order to permit of a certain draft of air. This cone, the lower diameter of which is nearly that of the building itself, hangs by a rope passing through the pulley C, and may, therefore, be raised or lowered at will. Lastly, the apparatus is completed with the fireplace D, outside of the building, and which contains a small cast-iron kettle E, in which the resin is placed. The operation begins by heating the kettle E, filled with resin. When the latter is melted, it is inflamed, and the incomplete combustion of the resinous vapors causes the formation of a quantity of large black flakes, which become attached to the cloths hanging in the room. The quantity of air necessary to the combus-

Fig. 59.



tion is regulated by a small sliding damper on the door of the fireplace. It is important to operate with the smallest quantity of air possible, otherwise the product will not be so abundant.

When the resin held in the kettle is burned out, another quantity is added, and the operation is continued for several days. When the black has accumulated in the room to such an extent that the operation cannot be continued, the apparatus is left to cool off entirely, in order to prevent the black from being inflamed by contact with the air. The cone C is then lowered, and in its descent scrapes off the black sticking against the sides. The black is removed through an iron door F, which is kept tightly closed during the operation.

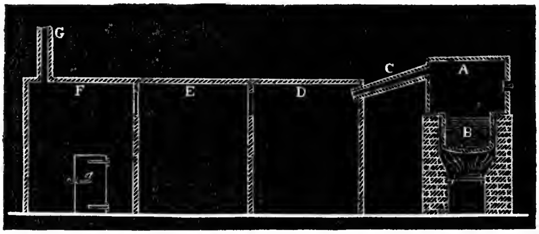
The black obtained by this process is used for marine and oil painting. It is much less pure when rosin waste is employed, since it contains a greater proportion of impurities which are carried over with it.

Second Process.—Tar Black.

The manufacture of lampblack by the incomplete combustion of coal tar, is cheaper than that we have just described. During the distillation of bituminous coal for making gas, there are produced considerable quantities of tar, which has several applications in the arts, one of which, and not the least important, is the preparation of lampblack.

The apparatus is a furnace A (Fig. 60), lined with firebricks, and which contains a small kettle B. A large and thick cast-iron pipe C is fixed to the upper part of A, and establishes a connection with a large condensing room, built of stone or brick, and divided into three compartments D, E, F, of unequal sizes. The black settles in these compartments, which communicate with each other by means of holes in the partition walls. The apparatus ends by a chimney G, about 1 metre high, which delivers into the atmosphere the uncondensable gaseous products.

Fig. 60.



The mode of operation is very simple: the furnace is first brought to a dark-red heat, and then the kettle B is put in. The tar introduced soon becomes inflamed, and produces an abundance of smoke which passes through the pipe C, and is condensed in the compartments D, E, F. A sliding register, in front of the furnace, allows of the watching of the operation. When the combustion of the tar in the kettle B is complete, a new quantity of material is added, and so on for several consecutive days. In order to render the combustion more rapid, the tar is now and then stirred with an iron hook. When the accumulation of charred residue in the kettle becomes too considerable, the kettle is removed, and is immediately replaced by a clean one filled with coal tar. One of the most essential conditions is to conduct the combustion with a minimum of air; otherwise, the yield will be less, and the product will have a russet, and sometimes a whitish tinge, which will depreciate its market value considerably.

The solid residue left in the kettles may be employed for heating the furnace at the beginning of an operation. It is very hard and compact, and requires to be removed with iron tools.

We have ascertained by experiments on a large scale, that 1000 kilogrammes of good coal tar will give on an average 250 kilogrammes of lampblack, that is, a yield of 25 per cent. The operation, with this quantity of material, takes six days, with one furnace and one man. The same man can attend to several fires at the same time.

When one furnace is used, the black is removed every week through the door *a*, which is hermetically closed during the operation. The packing of the 250 kilogrammes of black requires about 25 casks of 400 litres, or a cask for about 10 kilogrammes of black.

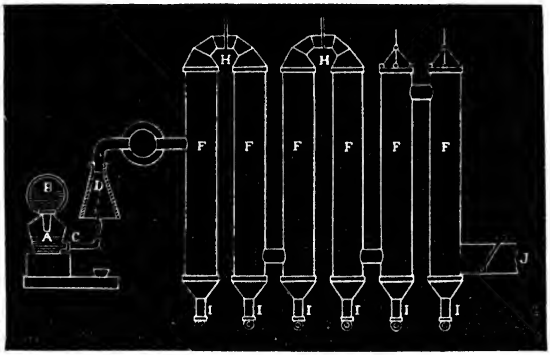
The tar should be free from earthy substances, or the yield will be less.

The same apparatus may be used for the preparation of lampblack, with the heavy (dead) oils of tar and schist. These oils, very rich in carbon, are very advantageous for this manufacture, and produce a very handsome black which is much esteemed. Lampblack is sometimes prepared from the soft pitch left after the incomplete distillation of coal-tar. This latter black is not much esteemed; but its quality may be improved by burning the pitch with the dead oils of tar and schist.

Third Process.—Oil or lampblack.

This black is the lightest and finest of all, and is obtained by burning certain kinds of oils, the vegetable ones preferably, in lamps of a peculiar construction. The apparatus is represented in Fig. 61.

Fig. 61.



A, lamp, the liquid level of which remains constant. It is fed from a reservoir B, filled with oil. At the lower part of A there is a bent tube C, the upper opening of which is on the same level as the oil in A. The combustion takes place with the aid of a wick made of cotton or amianthus. This latter substance is preferable, because it is incombustible, and may be used quite indefinitely. The flame burns under a cone D, fixed to an elbow-tube opening into a large horizontal pipe E. This pipe cools the smoke, and condenses the water, and other condensable liquid products, formed during the operation. From this pipe, the smoke passes through a series of large sacks F, F, F, six metres high, and one metre in diameter, which are kept open at the top and bottom by funnels of galvanized iron. The first and second sacks, and the third and fourth, are connected together by the curved metallic pipes H, H. The other connections at the top and bottom are through straight pipes. The lower funnels are closed by plugs I, I, I, which allow of the extraction of the black after each operation. The smoke condenses in these sacks, and the product is the finer as the oil itself is purer. The black condensed in the last sacks is also purer and finer than that in the first part of the apparatus, which is often somewhat wet and oily. Each series of sacks is terminated by a conduit J, communicating with a draft chimney for the escape of the uncondensable products. A damper regulates the draft, which should not be too strong or too weak. In the first case, the black in the sacks might become inflamed; in the second, the smoke could not pass through the whole apparatus.

The operation is very simple: the oil is kept at a constant level in the lamp, by keeping the reservoir B filled; and the damper is regulated so as to give sufficient air for the combustion.

The black is removed when a certain quantity has accumulated in the sacks. Receivers, barrels for instance, are placed under each funnel I, I, I, and, after taking off the plugs, the sacks are gently struck, so as to detach the black. In this manner, the various qualities of black may be collected separately, and we have already said that the product is the finer and the better as it is taken from the sacks further from the lamp.

Experience has proven that the same process may be applied to the combustion of the dead (heavy) oils of tar and schist. These oils are substituted for the vegetable ones, or mixed with them, in the lamps. The operation is conducted in the same manner. Of all the processes of manufacture we have described, this latter gives the purest black with the least waste, but it requires fluid materials.

Whatever be the mode of preparation, lampblack is never entirely pure. It holds fixed and volatile salts, fatty and oily substances, various pyrogeneous products, etc. It is purified by a calcination in thick sheet-iron cylinders, into which it is tightly packed, and which are heated in a reverberatory furnace. The cylinders may generally open in two parts by means of hinges, and it is then easy to remove the calcined black. But, as, after this operation, the product still contains various salts, it may be treated by dilute hydrochloric acid for ten or twelve hours. Several subsequent washings will remove the acid and the soluble salts. The black which has been purified in this manner contains but a trace of silicious matter, upon which the acid has no action.

We should state that the purification of lampblack is tedious and expensive, and that in the arts it is generally used as it comes from the producing apparatus.

§ 12. *Chrome or aniline black.*

Mr. W. H. Perkin has described a process for obtaining a coloring matter from a solution of sulphate of aniline, mixed with another solution of a bichromate. There is formed a black precipitate, which, being purified of certain brown impurities, may be used alone, or conjointly with lamp or ivory-black, for the preparation of printing inks, colors, and varnishes. This black is much more intense than lampblack, which always has a brown tinge.

For incorporating this aniline or chrome black with lampblack, Mr. J. R. Palmer uses 25 parts of chrome black, and mixes it with 75 parts of lampblack in a mill. The product is passed through fine copper gauze sieves, and is received in a leather bag. What remains upon the sieve is ground again. The chrome black may be used alone.

§ 13. *Various blacks.*

We shall conclude our remarks upon vegetable blacks by repeating that, for certain kinds of painting, a *charcoal-black* is employed, which results from the calcination in closed vessels of any kind of wood. This charcoal is very finely comminuted, and is washed in order to remove the soluble salts. It always possesses a bluish tinge.

Mr. W. E. Newton has recently published the details of a peculiar process for the manufacture of vegetable blacks, which are real ulmin-blacks.

"All the blacks," says he, "met with in the trade for painting, printing, etc., are slow in drying. This inconvenience is remedied by mixing with the carbon certain earthy or alkaline bases.

"The oxides of potassium, sodium, calcium, and aluminium may be employed in the preparation of the new blacks. The carbon is obtained from an organic substance, coal-tar, for instance, on account of its low price. The oxides are introduced, either in the caustic state, or as combinations, which may be mutually decomposed at the time of mixing.

"The following are the proportions for the mixtures: 100 kilogrammes of slaked lime are mixed with 80 kilogrammes of coal-tar, and then 9 kilogrammes of alum. The whole is made into a homogeneous paste, which is calcined in cast-iron retorts, like bone-black. When the carbonization is complete, the fire is removed, and the substances are left to cool in the closed retorts. Lastly, the black is removed, and is ready to be ground.

"By varying the proportions of tar and slaked lime, all of the tones and hues of gray and brown may be obtained."

The following is another mode of preparation of vegetable blacks, which is described in vol. 87 of the *Brevets d'Invention*, and which, notwithstanding all it claims, will probably furnish only an ulmin-brown.

The process consists in carbonizing any kind of vegetable matter, by the double action: first, of sulphuric and nitric acids, or of sulphuric acid alone; second, of heat. The action may be modified to suit the nature of the substances which are to be acted upon.

For instance, and in preference to other substances, we take the saccharine substance resulting from the transformation of potato starch by sulphuric acid. This syrup is dried, and mixed in an iron kettle with 12 to 15 per cent. of nitric acid, or 14 to 18 per cent. of concentrated sulphuric acid.

The mixture is stirred all the while, and is heated at from 100° to 110° C., which temperature is maintained for some time. Under the double action of the heat and acids, the substance becomes gradually thicker, and is converted into a black paste. The paste is brown when the operation fails.

When, from comparative color tests upon a plate, it is ascertained that the greatest intensity of black has been reached, there is added to the paste from 2 to 3 per cent. of concentrated sulphuric acid. The fire is urged more vigorously under the kettle, the contents of which are stirred all the time, in order to prevent them from sticking to the sides of the kettle. The mass soon becomes granular, when the heating is finished.

After cooling, the product is carefully washed in draining troughs. The black, thus obtained and dried, is of a perfect color, very light, and easily ground.

The process is also successful with ordinary flour, potato starch, or any amylaceous substance, with any ligneous or fibrous material, with rags, paper, wool, cotton, the leaves of trees, the pulp of beet roots, linseed cakes, etc., in fact with any carbonaceous substance. Nevertheless, we should prefer flour, potato starch, and the syrup of glucose, which we mentioned at the beginning.

The operator will easily ascertain, from the nature of the substance to be worked, how he should modify the proportions of nitric and sulphuric acids, and the degree of heat. An increased proportion of sulphuric acid will produce a more rapid and energetic carbonization, and the particles of black will be lighter and more divided. An excess of heat is to be avoided, because the substance, after being completely dried in the kettle, will become so hard that it will be difficult to pulverize it afterwards.

When the fluid syrup of potato starch (glucose) is employed, the acid present in it should not be neutralized with carbonate of lime or any alkali. The syrup is immediately concentrated by evaporation, and less sulphuric acid is to be mixed with it, since it retains that added for the saccharification.

The best substances for transformation into a fine black, are those which make transparent solutions with water. These substances are also those which are the more easily pulverized, and which absorb light more readily. Indeed, absorption of light, and black coloration are the same phenomenon.

This new black replaces lampblack, and those from ivory, bones, and charcoal. Therefore, it may be employed for the manufacture of printing ink, of that for copperplate printing, of blacking, of black paints, and of any other material requiring a durable black for a basis.

§ 14. *Inks.*

Inks, generally speaking, are the liquids employed for tracing those signs which represent human thought; but they are sometimes employed for dyeing and coloring various substances, wood for instance.

Inks have not a fixed and definite composition. They are principally, as is well known, a combination of a solution of sulphate of iron with a solution of nut-galls, in which the precipitate is kept in suspension by means of a gummy substance, which, moreover, improves the fluidity of the liquid.

Besides the two elements of the black compound, other ingredients are added in order to produce a more intense color, or a more pleasing hue, or peculiar properties, according to the uses for which it is intended.

Thus it is that we find formulæ for inks in which there are decoctions of logwood and other dye woods, alum, sugar, molasses, peroxide of manganese, alkalies or alkaline salts, acids, gelatin, soap, India ink, lakes, indigo, lamp and other blacks, alcohol, chloride of mercury, sulphate of copper, catechu and other tannin materials, essential oils, resins, isinglass, madder, salts of chromium, cobalt, and silver, etc. etc.

There are many other fluids of the same kind, some of which are the so-called indelible inks, for increasing the security of commercial transactions; others for writing with metallic pens; and lastly, those for marking linen, or for tracing colored signs or drawings.

Typography, copperplate printing, lithography, autography, etc., also use certain compositions called inks, and which are made of oil varnish, resins, balms, blacks, indigo, metallic salts, tallow, soap, wax, etc. etc.

We cannot here examine at length the preparation of these various products. Their composition, which varies *ad infinitum*, would require more room than can be had in this volume. We are, therefore, obliged to refer the reader to our *Manuel de la fabrication des encres* of the Encyclopedie-Roret, in which will be found all the formulæ which have been found advantageous in practice.

The manufacturer of colors may undertake the preparation of inks; but, generally in large cities, it forms a speciality.

C. ANIMAL BLACKS.

§ 15. *Bone blacks.*

The bones of animals are composed of water, fat, albumen, phosphates of lime and magnesia, carbonate of lime, and about 32 per cent. of an organic substance. When the bones are carbonized at a red heat in a closed vessel, the organic substance is decomposed into gases and volatile liquids, and the residue of carbon, mixed with the earthy salts, forms animal or bone black. Before carbonizing the bones, they are boiled in order to remove the fat. The carbonization is done in closed vessels, and retorts, and the cold product is ground and passed through silk sieves.

Bone black has generally a reddish reflex, which is believed to be due to the phosphate contained in it, and which may be partly removed by a treatment with hot and dilute hydrochloric acid. After rinsing with water, the black is calcined a second time.

§ 16. *Ivory black.*

This black is obtained by calcining ivory scraps in a clay crucible with its cover luted on, in such a manner, however, that the gases may escape. The crucible is brought to a red heat, and the operation is complete when gases cease to burn at the junction of the crucible and its cover. After a thorough cooling, the black is powdered.

Thus prepared, this black is of the first quality for painting. It is brought to a great degree of comminution by grinding with water, either with a slab and muller, or between two horizontal stones. The grinding should be continued until the paste is perfectly smooth and homogeneous. The black is then poured into convenient moulds, and dried first at the ordinary temperature, and afterwards in stove-rooms heated to from 80° to 100° C.

We should state that most of the black sold as ivory black, is only a bone black of the first quality.

§ 17. *Candle black.*

Candle black is very light and of a splendid and intense color. It is prepared by burning candles made of animal substances, stearin preferably, under metallic plates or funnels. When a certain proportion has accumulated, it is collected delicately, so as not to compress it, and so as to preserve its lightness.

§ 18. *Prussian black.*

This is the product of the calcination of Prussian blue in closed vessels. This black is costly, but little employed, and advantageously replaced by ivory and lampblacks.

§ 19. *China or India ink.*

This is a composition, the basis of which is the finest and purest lampblack. The calcined oil or lampblack is that preferred for this manufacture, and gives an ink of the first quality, which is much employed as a water color. It is used in England for mezzotinto engravings, and the hue is heightened by a small proportion of carmine lake. This ink was discovered in China, and the inhabitants of that country had for a long time the monopoly of its manufacture. But since the development of chemistry and the arts, this product has been perfectly imitated. Among the numerous formulæ indicated for its preparation, we find that the following one gives a product in no way inferior to the best China ink:—

Calcined lampblack	100	grammes.
Shale black (Boghead) in impalpable powder	50	"
Indigo carmine in cakes	10	"
Carmine lake	5	"
Gum Arabic (first quality)	10	"
Purified ox-gall	20	"
Alcoholic extract of musk	5	"

The gum is dissolved in 50 to 60 grammes of pure water, and the solution filtered through a cloth. The indigo carmine, lake, lampblack, and shale black are incorporated with this liquor, and the whole is ground upon a slab with a muller, in the same manner as ordinary colors, but in this case the grinding takes much longer. When the paste is thoroughly homogeneous, the ox-gall is gradually added, and then the alcoholic extract of musk. The more the black is ground, the finer it is. For the above quantities, the grinding should last at least twelve hours.

The black is then allowed to dry in the air, until it has acquired sufficient consistency to be moulded into cakes, which, in their turn, are still further dried in the air, out of the reach of dust. When quite firm, these cakes are compressed in bronze moulds having appropriate designs engraved on them. The moulded ink is then wrapped in tinfoil, with a second envelope of gilt paper.

The ink which has been prepared in this manner possesses all the properties of the real Chinese article. Its grain is fine and smooth; it flows very well, mixes perfectly with many other colors, and becomes so firmly fixed to the paper, that other colors may be spread over it without washing it out.

Gum Arabic might be replaced by gelatin; but as this latter substance is easily decomposed and putrefied, we prefer gum Arabic. Moreover, the ink is better, and flows more easily upon the paper.

SECTION VI.

GREEN COLORS.

§ 1. *Green Verona earth.*

There are found in Italy, near Verona, in France, Germany, Hungary, and the island of Cyprus, certain earthy masses which are inclosed in the amygdaloid, porphyric, and basaltic rocks, and which possess a Céladon green color when seen in masses, and are a light green when powdered. They are smooth to the touch as are all magnesian earths, and smell like clay. Such is the physical appearance of Verona earth, which was used as a pigment by the Greeks and Romans, and which, at the present time, is washed and employed for landscape painting on account of its durability.

Two kinds of Verona earth are found in the trade: that from Verona, and that from the island of Cyprus. The Verona article is of a purer color, and has been analyzed by Mr. Berthier, and more recently by Mr. Delesse. Its composition is—

Silica	51.21
Alumina	7.25
Protoxide of iron	20.72
Magnesia	6.16
Soda	6.21
Water	4.49
Protoxide of manganese	trace.

The earth from the island of Cyprus has a color intermediary between verdigris and apple-green. Its analysis by Klaproth gives—

Silica	51.5
Protoxide of iron	20.5
Potassa	18.0
Magnesia	1.5
Water	8.0

There are many natural green substances, which could be employed in the arts, and which possess tones or hues different from that of Verona earth. For instance, Poland earth is a leek-green; that from Unghvar, resulting from the decomposition of trachytes, is a grass-green. Small granules of green earth are found disseminated in the coarse limestones of the lower marine deposits, in the neighborhood of Paris.

§ 2. *Malachite.*

This green substance is found principally in Siberia, in the Oural Mountains, and in the Bannate, in the Tyrol, in Saxony, Bohemia, England, etc. It is a native hydrated carbonate of copper which possesses different hues. It is also called *mountain green* and *Hungary green.* Reduced to a very fine powder, this substance gives a magnificent green, which is, however, too expensive to be largely used. It has been advantageously replaced, first, by the greens of Brunswick and of Bremen, and afterwards, by that of Schweinfurt and by Mittis green, which are more durable than the two former. The manufacture of these artificial greens will be described further on.

§ 3. *Iris-green.*

Iris-green is a color which was formerly used for miniature painting; but it is so fugitive that it has been abandoned. It was prepared with the flower of the iris, macerated in alum or gum-water. The solution was filtered, and evaporated in dishes, in a dark place.

§ 4. *Sap-green.*

Sap-green is a dark green mass, which is employed only for water colors and the manufacture of pastels. It is prepared at Nuremberg and in the south of France. We reproduce here the improvements made by Mr. R. de Hagen, and which are described in the *Technologiste,* vol. xiv. page 415.

"Sap-green, or vegetable green, is the juice of the buckthorn berry (*Rhamnus catharticus*), and is prepared by various processes, which do not always produce a handsome green, but often result in a greenish-yellow color, or a dirty yellow, or a grayish-yellow. The green-yellow coloration is generally due to the employment of quite ripe berries, and the grayish or dirty yellow to these same berries after they have passed their maturity. It happens sometimes that sap-green, when put upon a brush, is wanting in transparency, and this is due to an addition of carbonate of magnesia. This color is often sticky and viscous, because carbonate of potassa has been mixed for rendering the juice green. Lastly, there are now to be found in the trade more or less brown sap-greens, because they have been evaporated at too intense a heat.

"All of these properties of various kinds of sap-green are often united in a greater or less degree in the same sample of green, which is none the better for it. For instance, there is often sold, under the name of sap-green, a yellowish substance, rendered opaque by the presence of magnesia. If potassa be added, it remains shiny and yellow, and is altered when spread with the brush. Lastly, certain peculiarities of sap-green are due to the proportions of its constituent parts.

"As I have had the opportunity of learning several processes for the manufacture of sap-green, and of experimenting upon them, I think that it may be useful to give some particulars as to the manner of preparing a very fine quality of this color.

"In order to prepare a fine sap-green of a decidedly green color and translucent, the berries employed should not have reached their complete maturity. Their juice will, therefore, not appear entirely blue, but somewhat greenish. The boiling of the berries and the evaporation of the juice should be done at a moderate temperature. A charcoal fire may be employed at the beginning, but the evaporation must be finished upon a water bath. Lastly, the green color will be made apparent by means of the double sulphate of alumina and potassa (potassa alum), because this salt produces the finest color, gives a good consistency to the mass, and preserves the transparency of the color when spread with a brush. Such are the main conditions in the preparation of a good sap-green; and as it is important to know the proportions, we give as a formula the following directions:—

"Any given quantity of buckthorn berries, not entirely ripe, are boiled with a small proportion of water in a clean copper kettle, and upon a moderate charcoal fire. The mass is continually stirred, until it has become a kind of magma, which is pressed through cloths. The residue is washed and pressed again. The liquors are left to settle, and are filtered through flannel bags, before being evaporated to the consistency of a thick extract, upon a gentle fire.

"The thickened juice is then weighed, without pouring it out from the kettle (the weight of which is known), and to every kilogramme of liquor, there are added 65 grammes of alum dissolved in water, and the mixture is thoroughly stirred all the while. The evaporation is completed upon a water or steam bath, and continued as long as practicable without altering the color. The product is then poured into calf bladders, and dried in the air.

"A sap-green, prepared in the aforesaid manner, appears black when viewed in masses, and a fine green by looking at the edges. Spread with a brush it remains transparent, dries rapidly, and produces a handsome leaf-green. Exposed to the air, it does not become damp. To sum up, it presents no inconveniences, and is all that can be desired.

"By varying the proportions of alum, different tones of green will be obtained. On the other hand, should it be desired to have a yellowish-green, the riper the berries the more yellow the color.

"Since alum gives us the means of producing the finest qualities of sap-green, we should reject all the other substances previously employed, such as magnesia, lime, potassa, etc., because their products are always defective for one reason or another."

§ 5. *Picric acid green.*

Mr. V. Stein, Professor at the Polytechnical School of Dresden, sends us a few particulars regarding this color.

"The manufacture of artificial flowers has already for some time employed a green of various tones and hues, which equals and even surpasses the finest Schweinfurt green. Analysis shows that the blue and yellow elements of this green are: the first, the blue of the sulpho-indigotate of potassa (carmine of indigo); and the second or yellow, picric acid, also called carbo-azotic, binitro-phenic acid.

"Therefore, by mixing solutions of picric acid and of indigo carmine, there is obtained a very fine green, in which a certain proportion of gum Arabic may be dissolved. It is probable that, when this green is more widely known, it will replace the Schweinfurt green in the manufacture of paper hangings, at least of those where the cost is a secondary consideration."

§ 6. *Bremen green. Bremen blue. Verditer blue and green.*

Mr. J. C. Habich has published in the *Technologiste*, vol. xvii. p. 413, very complete data on the manufacture of this color, which was previously but imperfectly known. We here reproduce the article.

"There is found in the market, under the names of blue and green verditer, Bremen blue, Bremen green, a pigment which is a hydrated oxide of copper, more or less pure. This color, prepared for the first time by Kulenkamp and Hoffchlaeger, of Bremen, has been manufactured by several methods, which are not without influence upon the principal properties of the product.

"The hydrated oxide of copper, prepared by precipitating a neutral and soluble salt of copper, always forms, in drying, a dense mass with a conchoid fracture. On the other hand, basic and insoluble copper salts, when treated by alkalies, furnish porous and pulverulent colors. In accordance with the acid of the copper salt and the process followed, the color presents more or less variable properties, the knowledge of which is useful to the consumer, and which should certainly be attributed to the different modes of preparation.

"In the beginning, a basic chloride or oxychloride of copper was always employed, and although the preparation of this compound with metallic copper (old ship sheathing) was done by different processes, there was no difference in the properties of the finished color. But it is absolutely necessary that the pale green magma should contain no subchloride of copper. Let us now examine carefully some of these modes of manufacture, in order thoroughly to understand the importance of the condition we have just stated.

"There are mixed in large wooden tubs, in the construction of which there should not be a single iron nail—

"1. 100 parts of old copper sheathing, 99 parts of powdered sulphate of potassa, and 100 parts of chloride of sodium (common salt). The whole is moistened with pure water.

"2. 100 parts of copper, 60 of common salt, and 30 of sulphuric acid, which latter has been diluted with three times its volume of water.

"3. Or there is poured upon the copper a solution of oxide of copper (copper scales) in pure hydrochloric acid.

"In the first case there is obtained a chloride of copper, which, in contact with more metal, becomes a subchloride. This salt, by the absorption of the oxygen of the air, is transformed into the basic green compound called in the factories oxide.

"In the second case, the hydrochloric acid set at liberty, and the oxygen of the air, produce the same effects, and the same basic salt is obtained.

"The third case is explained in the same manner.

"Now, as the subchloride of copper (Cu^2Cl), decomposed by caustic alkalies, precipitates an orange-yellow suboxide of copper (Cu^2O), it is evident that there should remain no trace of this subchloride.

"On that account, in several factories, it is customary to prepare the magma of basic oxychloride one year in advance, and to stir it frequently before it is used. This process is expensive, since the interest of the capital is lost. The same result is obtained by entirely drying, now and then, the wet mixture. In this manner atmospheric air penetrates the mass, and oxidizes it thoroughly.

"During the transformation of this green magma into a hydrated oxide of copper, an interesting phenomenon takes place. If this magma be introduced by degrees into a caustic lye of potassa or soda, marking about 20° Bé., the product, after a thorough washing and drying, is highly comminuted, covers a great deal, and becomes darker by the addition of a very small quantity of water. If the magma be diluted with an equal volume of water, the mixture then poured at once into an excess of caustic lye, and the whole rapidly stirred and then let to rest, a few minutes will be sufficient for the materials to form a mass, which can scarcely be divided. After a complete washing and drying, the color is much lighter than the former one, but it covers less. Instead of turning darker by a drop of water, the wet spot becomes a grayish-white, which disappears on drying.

"If it be attempted to blue the precipitate of hydrated oxide of copper, obtained by any of the above processes, the product will not be satisfactory, since the color will be without intensity or freshness. On the contrary, a good result will be obtained by adding to the magma, before its treatment with the alkaline lye, a small proportion of a concentrated solution of sulphate of copper. It appears that there is a highly basic sulphate of copper, which deepens the color; and all such colors, worked in this manner, contain a small amount of sulphuric acid and of alkali (from the lye used).

"A product, covering well, can be prepared as follows: To 100 kilogrammes of the thick magma of basic oxychloride, add a concentrated solution of 7 kilogrammes of sulphate of copper, and then 40 kilogrammes of a concentrated caustic lye (32° to 36° Bé.). Stir the mixture vigorously and rapidly, and pour it into about 150 kilogrammes of caustic lye, marking 20° Bé. The decomposition is thus complete, and the precipitate is carefully washed. Before the color is received upon the filter it is passed through a fine hair sieve. Desiccation at a high temperature should be avoided, so as not to change the hydrated state of the copper oxide. It is no less important that the air passing through the stove-room should be pure and free from acid and sulphuretted fumes.

"The process which we have just described is, with slight modifications, nearly everywhere followed. But, in the following lines, I will indicate another method, which is to be highly recommended to color manufacturers.

"When neutral nitrate of copper is decomposed by an insufficient proportion of a solution of carbonate of potassa, the flocculent precipitate of carbonate of copper formed at first is gradually transformed into a subnitrate of copper, which precipitates in the shape of a heavy green powder. If this basic salt of copper be treated by a solution of oxide of zinc in potassa, there is formed a dark blue color, which is extremely light, and with great covering power. It appears to be a zincate of copper, with a very small proportion of a highly basic nitrate of copper.

"In order to render this process practical, the operation will be conducted as follows:—

"Copper scales are calcined in a reverberatory furnace or a muffle, until all the suboxide (Cu^2O) is transformed into protoxide (CuO), that is to say, until a sample dissolves in nitric acid without the production of red nitrous vapors. If the nitric acid contains hydrochloric acid, which is often the case, the silver which may be present in the copper scales will be precipitated in the form of chloride, and may then be collected.

"The solution of nitrate of copper is heated and decomposed by a clear solution of carbonate of potassa. As soon as the effervescence diminishes in intensity, the solution of carbonate of potassa is added by small quantities at a time, until there remains but little undecomposed copper in the solution. In order to collect this remainder of metal, the clear liquor is decanted, and the green precipitate is washed several times with small quantities of water. All the liquors are collected, and the remaining copper is precipitated by a solution of potassa. The green carbonate of copper is introduced into a new solution of nitrate of copper, in which it is transformed into a basic salt. The previous liquors are evaporated, and leave crystals of nitrate of potassa.

"An economical solution of oxide of zinc is made as follows: Clippings of metallic zinc are treated in a cast-iron vessel with a caustic solution of potassa or soda. Hydrogen is immediately disengaged, and the alkali becomes saturated with the oxide of zinc, which plays the rôle of an acid. When the liquor is clear, it is employed for the decomposition of the basic nitrate of copper. The product is a handsome and light Bremen blue, and the evaporated liquor, when potassa has been used, gives crystals of nitrate of potassa.

"The advantage of this process is based principally upon the preparation of a cheap nitrate of copper (since nitric acid may at a moderate cost be extracted from nitrate of soda), and upon the production of nitrate of potassa, which is a valuable secondary product."

§ 7. *Brunswick green.*

Hydrochloric acid can be had at a very low price in certain localities, and is used for extracting the copper from poor oxidized ores. Nevertheless, this acid has scarcely any effect upon those ores which are not oxidized, and it is necessary to add now and then a small proportion of nitric acid. A cheaper process consists in moistening the ore with hydrochloric acid, and exposing it to the contact of the atmosphere. The metal then becomes easily attacked by chlorine, and even by solutions of chloride of ammonium and of common salt. The subchloride produced is rapidly transformed into oxychloride, and forms a fine light green called Brunswick green.

§ 8. *Scheele's green.*

Oxide of copper, combined with various substances, produces quite a number of green colors, which, unhappily, are highly poisonous, but possess great brightness. The oldest of these colors is a neutral arsenite of copper, discovered in 1778 by Scheele. The formula as given by the illustrious Swedish chemist is as follows:—

Dissolve, in a copper kettle, 1 kilogramme of pure sulphate of copper in 20 litres of water. In another vessel prepare an arsenite of potassa by boiling 1 kilogramme of carbonate of potassa and 325 grammes of arsenious acid in 6 litres of water. These two solutions are filtered, and while they are still hot, the arsenite of potassa is slowly poured into the solution of sulphate of copper, which is stirred all the while. The precipitate of arsenite of copper settles in the liquor, which has become a solution of sulphate of potassa. This is decanted, and the precipitate is carefully washed with hot water, drained upon a cloth, and dried at a low temperature. The product is about 1200 grammes of a fine green color.

This product, we have already said, is a neutral arsenite of copper; but it may be rendered basic by increasing the proportion of sulphate of copper. The color is finer, but not so durable.

In the process actually followed by manufacturers, a solution holding at the same time arsenious acid and the sulphate of copper, is precipitated by one of carbonate of potassa, which is added by small quantities at a time, until the color has acquired its greatest brightness. The liquors are stirred during the whole precipitation.

Scheele's green may be used with water or oil, and was formerly much employed especially in the manufacture of paper-hangings. It is now replaced by Schweinfurt green, which has more durability.

Another sort of Scheele's green, called *green lake*, is prepared in this manner: A solution is made of 1 kilogramme of tartrate of potassa and 600 grammes of arsenious acid in 8 litres of water, which, after filtration, receives a solution of sulphate of copper poured slowly in. The mixture is kept stirred all the while. After settling and decantation, the precipitate is washed with clear and cold water, and dried in the stove-room.

§ 9. *Schweinfurt green.*

Schweinfurt green is a combination of acetate and arsenite of copper, the color of which varies from a dark to a pale green, and which is employed in all kinds of painting and in the manufacture of paper-hangings. There are several processes of manufacture which we shall indicate.

First Process.

This process is due to Baron Liebig, and is as follows: One part of verdigris is heated in a copper kettle with sufficient distilled vinegar to be dissolved, then one part of arsenious acid, dissolved in water, is added. The mixture of these substances produces a dirty green precipitate, which is dissolved in a new quantity of vinegar. After boiling for some time, a new precipitate appears, which is granular, crystalline, and of a magnificent green. It is separated from the liquor, carefully washed, and drained.

If the liquor still contains copper, arsenious acid is added; and conversely, if arsenious acid be in excess, acetate of copper is introduced. Lastly, should it contain an excess of acetic acid, it is used again for dissolving verdigris.

In order to deepen and brighten the color of the product, which is slightly bluish, it is boiled with one-tenth of its weight of commercial potash.

Second Process.

This Schweinfurt green is prepared by mixing 10 parts of acetate of copper with a sufficient quantity of water, heated at 50° C., to make a liquid and homogeneous magma, to which is added a solution of 8 parts of arsenious acid in 100 parts of boiling water. The whole is kept boiling. It is sometimes necessary to add a small quantity of acetic acid to the mixture, in order to obtain a finer color with a crystalline appearance. The precipitate is collected upon a filter, drained, and dried.

The decanted liquor is advantageously used for dissolving the arsenic of a new operation. The solution will be facilitated by the addition of carbonate of potassa, which forms an arsenite of potassa.

Third Process.

This process has been described by Mr. Braconnot, who prepares the green as follows:—

Dissolve 6 parts of sulphate of copper in a small quantity of hot water, and prepare another solution by boiling in water 6 parts of arsenious acid with 8 parts of commercial carbonate of potassa. When carbonic acid is no longer disengaged, the two liquors are mixed while being stirred. There is formed an abundant precipitate of a dirty greenish-yellow color, which, by the addition of a slight excess of acetic acid, becomes crystalline and of a fine green. It is washed with boiling water, collected, and dried.

Fourth Process.

This process is due to Mr. Wingens, a manufacturer of colors. From 9 to 10 kilogrammes of arsenious acid are dissolved in hot and pure water, and 500 grammes of potassa are added to it. After stirring, and settling for a few hours, the precipitate is collected upon a cloth. (The author has omitted to indicate the proportion and the kind of copper salt necessary to produce the above precipitate.—Trans.)

There are probably other processes for obtaining different tones and hues of this green, which are caused by varying the proportions of the materials, or by other substances added fraudulently or otherwise. A pure Schweinfurt green is entirely soluble in nitric or hydrochloric acid.

The commercial sulphate of copper generally used for the manufacture of arsenical greens is often contaminated with sulphate of iron, which considerably impairs the purity and the brightness of these colors. Mr. A. Bacco has indicated a simple and economical process for removing the iron from solutions of sulphate of copper. A gelatinous precipitate of carbonate of copper is produced by decomposing a solution of sulphate of copper with one of carbonate of soda. The precipitate is washed, and a suitable quantity of it is added to the solution of sulphate of copper to be purified. After stirring, the mixture soon deposits flakes of oxide of iron, and the clear liquor contains only a pure sulphate of copper.

§ 10. *Mittis green. Vienna green. Kirchberger green.*

Mittis green is an arseniate of copper, which is prepared by dissolving 20 parts of arseniate of potassa in 100 parts of hot water, and mixing this solution with another of 20 parts of sulphate of copper. During the whole operation the mixture is stirred. There is formed a pulverulent precipitate of a light-green or grass-green color, which is washed and dried. By varying the proportions, several tones and hues are produced. But in the commercial article these variations are generally due to the introduction of foreign substances.

The arseniate of potassa is prepared by boiling arsenious acid in concentrated nitric acid, filtering, and saturating with carbonate of potassa, and crystallizing the arseniate.

§ 11. *Green ashes.*

These green ashes are prepared as follows: 1 part of caustic lime and 2 parts of arsenious acid, with a sufficiency of water, are boiled together. This solution of arsenite of lime is decanted or filtered clear, and, while it is still hot, it is stirred at the same time that it receives a solution of sulphate of copper. The precipitate is a green powder of sulphate of lime and of arsenite of copper, which is washed and dried.

Green ashes are used only for coloring prints, since they do not possess sufficient body for oil colors.

§ 12. *German green without arsenic.*

For some time past there has been sold in Germany a *green without arsenic*, which is intended as a substitute for the arsenical Schweinfurt green. This color is not so bright as the latter, is in the shape of light and crumbling cubes, and may be applied to many purposes, although it is poisonous.

We are not acquainted with the preparation of this color. An analysis made by Mr. C. Struve shows its composition to be—

Chromate of lead	13.65
Basic carbonate of copper	80.24
Oxide of iron	0.77
Carbonate of lime	2.65
Water	2.58
	99.89

This green is very durable, and has more body than Schweinfurt green.

§ 13. *Erlaa green.*

According to Mr. Weilhem, Erlaa green is prepared in the following manner, in a small town of Saxony which bears that name.

Pure sulphate of copper and 30 per cent. of its weight of common salt, are dissolved in water. 100 parts of this solution are poured into a milk of lime, composed of 300 parts of water, and from 40 to 50 parts of white and well-burned lime. As soon as the blue color appears there are added from 8 to 12 parts of a soluble chrome salt, the neutral chromate of potassa being preferred. The color is washed with water, and immediately pressed.

Other copper salts, or a greater or less proportion of lime or of chromic salt, will result in a great variety of hues of this color.

§ 14. *Mineral green.*

This color is but little used in the arts, because it does not cover enough. It is a mixture of hydrated oxide of copper with a greater or less proportion of arsenite of copper. It is prepared by precipitating, with caustic potassa, a solution of sulphate of copper and 12 to 15 per cent. (of the weight of the sulphate) of arsenious acid (white arsenic). If, as Mr. Habich advises, there be added to the precipitate a solution of zincate of potassa, prepared in the manner previously explained (see Bremen green or Verditer), there is obtained a very bright and not too expensive color of a light green. 100 kilogrammes of copper (sulphate of?) and 15 kilogrammes of arsenious acid and alkaline zincate, furnish 93 kilogrammes of color.

Another mineral green of an apple-green color, with a bluish reflex, covering and drying well, but turning black easily, is prepared from a mixture of 2 parts of Scheele's green, 6 parts of white lead, 2 of black oxide of copper, 3 of mountain blue, and one-half part of neutral acetate of lead.

§ 15. *Paul Veronese green.*

We are not acquainted with the mode of preparation of this fine and durable color. It is another arsenite or arseniate of copper, made in Alsace and in England, high in price, and used either for water or oil painting.

§ 16. *English green.*

English green, of which there are innumerable varieties in the trade, is a Scheele's green mixed, while in paste, with sulphate of baryta or sulphate of lime, tempered with a small quantity of water. Its hue varies from an apple-green to that of a dead leaf. It is employed with water and oil, but generally alone, because it alters other colors.

§ 17. *Neuwied green.*

A. 16 parts of sulphate of copper, dissolved in hot water, are decomposed by a solution of arsenious acid. On the other hand, 4 parts of well-burned lime are slaked, and mixed with cold water, so as to make a milk of lime, which is poured through a fine hair sieve into the arsenical solution of copper, the latter being kept constantly stirred. The resulting green color is washed several times. Other qualities of this pigment are prepared by the following recipes:—

B.	Sulphate of zinc (copper?)	8.000	kilogrammes.
	Arsenious acid	1.250	"
	Lime	1.000	"
C.	Sulphate of copper	8.000	"
	Arsenious acid	0.750	"
	Lime	2.000	"

The color called *pickel grün* in Germany is prepared in the same manner, with a proportion of arsenious acid equal to 3.750 to 4.000 kilogrammes.

§ 18. *Milory green. Silk green. Green cinnabar. Leaf green.*

The real mode of manufacture of this fine color is still unknown. It is found in the market in the shape of troches, it unites with other colors well, and is employed for oil painting. It is imitated to a certain extent, by mixing together, and in certain proportions, ferrocyanide of potassium, sulphate of iron, acetate of lead, and chromate of potassa. A few chemists certify that there is also some sulphate of baryta.

These greens, according to Mr. Arnaudon (*Technologiste*, vol. xx. p. 519), are intimate mixtures of chrome yellow and Prussian blue, with an addition of alumina, or of other neutral and colorless bases or salts. These greens possess a certain brightness and great body, but they participate in the inconveniences of binary colors (mixtures of two simple—primary—colors, yellow and blue, in this case), that is, their color changes and their brightness diminishes under artificial light. These greens, moreover, do not resist alkalies, which destroy the blue and produce a brown-yellow. Acids, by the destruction of the chrome yellow, render the blue predominating. They are altered by solar light, and darken by the action of the sulphur held in other pigments, such as vermilion, orpiment, etc., with which they may be mixed.

Prussian green is a color which is prepared by pouring a solution of ferrocyanide of potassium, into one of a soluble cobalt salt (nitrate, sulphate, chloride). Its hue is very rich, but readily turns to a reddish-gray.

Binary mineral greens, more durable than the preceding, may be prepared from mixtures of the yellows of sulphide of cadmium, Naples yellow, and the chromates of baryta, tin, and zinc, with the blues of ultramarine and of cobalt. They are not blackened by sulphuretted gases.

§ 19. *Green of stannate of copper.*

The color of this green, in the opinion of Mr. Gentele, is not inferior to that of arsenic greens. Among the many formulæ given for its preparation, the following is one which gives a good product:—

To a solution of 125 parts of sulphate of copper in pure rain-water, there is added a solution of 59 parts of tin in nitric acid. This mixture is precipitated by an excess of caustic soda. The green color is washed and dried.

A less handsome green is prepared as follows:—100 parts of nitrate of soda, and 59 parts of tin, are brought to a red heat in a Hessian crucible. When the mass is cold, it is dissolved in a dilute caustic lye. This solution is allowed to become clear, when it is diluted with more water, and poured into a solution of sulphate of copper. The reddish-yellow precipitate, soon becomes of a handsome green, by washing and drying.

§ 20. *Elsner green.*

This copper-green, in which there is no arsenic, is not so bright as those of arsenic. Nevertheless, the various hues found in Germany are good pigments, which are not entirely devoid of brightness, and are less dull than green ultramarine.

These green colors are prepared by pouring a decoction of yellow wood, clarified by gelatin, into a solution of sulphate of copper, and adding to the mixture from 10 to 12 per cent. of tin-salt (protochloride of tin). The whole is precipitated by an excess of caustic potassa or soda. The deposit is thoroughly washed, and its green color acquires a bluish tinge by drying. A more yellowish hue is obtained by increasing the proportion of yellow wood.

§ 21. *Green cinnabar.*

We have already indicated, in the article on chrome yellows, the preparation of a green color, which is a mixture of chrome yellow with Paris blue. There is sold in Germany, under the name of green cinnabar (*Grüner zinnober*), a color of the same kind and without arsenic, the hue or tone of which varies from a dark to a light green. Mr. L. Elsner recommends the following mode of manufacture:—

A solution of yellow chromate of potassa is mixed with another of ferrocyanide of potassium (yellow prussiate of potassa). Another separate mixture is made of neutral acetate of lead, and of proto-acetate of iron, which is prepared by decomposing a solution of subacetate of lead with one of sulphate of iron.

By the reaction, an insoluble sulphate of lead is formed, and the proto-acetate of iron remains in the solution. It is the clear liquor which is used; but this acetate of iron may be prepared by other processes.

The first mixture is poured into the second, and there is formed a more or less dark precipitate, which is washed and dried at a low temperature. Dark tones are obtained by having the iron and the ferrocyanide predominating; and the light ones by an excess of lead and of chromate.

§ 22. *Green lakes. Vegetable green. Grass-green. China green.*

A green lake is generally a color prepared with the lake of a yellow coloring substance, mixed with Prussian blue. These pigments give very handsome colors, which, however, in a majority of cases, possess but slight durability.

The green lakes and the vegetable greens, according to Mr. Arnaudon, may be divided into three categories.

The first of these categories comprises the compound greens, formed by the mixture of a vegetable blue and a mineral yellow, and conversely. For instance, indigo-carmine with the yellows of chrome, Naples, Cassel, Verona (oxychloride of lead), orpiment, and cadmium. These greens, especially those in which the yellow is a chromate or a sulphide, are easily altered by some oxidizing or reducing action. In the converse case, that is, when the blue is of mineral, and the yellow of vegetable origin, for instance, Prussian blue, molybdenum blue, ultramarine blue, etc., associated with gamboge, stil-de-grain, woad, etc., we have still to fear the mutual alterations of the two component colors. Thus, Prussian blue, in contact with an organic substance, turns by degrees to a black, while the mixed yellow becomes brown. Ultramarine itself becomes paler, if the yellow develops any acidity. In regard to the green with molybdenum blue, the destruction of the color is ordinarily due to an oxidation of the molybdenum compound.

The second category is composed of the compound greens resulting from a mixture of vegetable yellows and blues; for instance, indigo blue with woad yellow, Indian yellow, and the yellows of *gardenia* and *broussonetia*. Although these greens cannot be considered fast colors, they are nevertheless superior to the preceding ones from the harmony in their lighter tones and hues. The more solid greens of this category are those formed of indigo, associated with the yellows of Persian berries, woad, and gardenia, and Indian yellow.

In water color painting, it is possible to employ a mixture of picric acid, or of picrate of ammonia with indigo carmine. But this green is not durable, and painting exposed to solar light for several months becomes yellowish, then yellow, and lastly, russet, from a mutual decomposition of the picric acid and indigo.

In the third category of vegetable lakes we have the green lake, made of a naturally green coloring substance, united to a colorless metallic oxide. For instance, grass-green is chlorophyl associated with lime; sap-green is the coloring substance extracted from the bark or berries of the buckthorn, and precipitated by lime or alumina. China green is to be added to the list, although it is still too expensive to be used for ordinary paints.

This last green, in daylight, presents nothing extraordinary, and its bluish-green hue makes it resemble green ultramarine. But, under artificial light, it acquires a brightness and a purity of color, which, united to its perfect solubility, renders it a precious dye for those tissues which are intended to shine under artificial light. This green stands quite well the action of the air, but to a much less extent than indigo, and does not well resist the influence of alkaline fumes. Acids change China green to a violet-blue.

§ 23. *Mineral green lake.*

This lake is a mixture of the oxides of copper and zinc, which is prepared by precipitating with carbonate of potassa a saturated solution of copper in 1 part of nitric acid and 3 parts of hydrochloric acid, to which is added a solution of zinc in concentrated nitric acid. The light green precipitate of the two carbonates is washed, dried, powdered, and heated in a crucible, until the carbonic acid is expelled, and the product has acquired a fine greenish hue. This pigment, misnamed mineral lake, is ground very fine; and is employed for water and oil colors. It is very durable.

§ 24. *Rinmann green. Cobalt green. Zinc green.*

Rinmann green is a combination of oxide of zinc with oxide of cobalt. It is prepared by dissolving 500 grammes of cobalt ore, as pure as possible, in 4 kilogrammes of concentrated nitric acid, and adding a solution of 1 kilogramme of zinc in 5 kilogrammes of nitric acid. The mixture is diluted with water, and then precipitated by a solution of carbonate of potassa. The pink-white precipitate is washed upon a cloth, dried, and calcined in a crucible at a high temperature. The product is very durable, and of a fine green color.

Mr. R. Wagner, who has examined the preparation of Rinmann's green, expresses himself as follows, in a note published in the *Technologiste*, vol. xviii. page 409:—

"Rinmann green, or cobalt green, is a color discovered towards the end of the last century by the Swedish chemist Rinmann. It is obtained by the calcination of a mixture of oxide of zinc and of oxide of cobalt. It is not so much on account of a want of beauty in the color, as because the constituent parts are expensive, that this green pigment has not been extensively employed. Even now its description is found only in chemical books, and the color has a place only in collections of chemical preparations.

"Of late years, since zinc has become cheap, and a sufficiently pure oxide of cobalt may be had at a moderate price, the conditions of the manufacture of cobalt green are more favorable. I have, therefore, undertaken a series of experiments on the best manner of preparing this pigment, and I will now give the results of my researches.

"The first condition, which is indispensable, is to prepare a protoxide of cobalt as free as practicable from foreign metals. For this purpose the oxide of cobalt sold by certain manufacturers of blue in Saxony (Oberschlemma, Pfannenstiel) is used. It is dissolved in 3 parts of hydrochloric acid, and the solution is evaporated to dryness. The residue is dissolved again in 6 parts of water, and a stream of sulphuretted hydrogen is passed through the liquor as long as precipitation takes place. The clear liquor, decanted from the sulphides of the foreign metals, is again evaporated to dryness, and the residue is dissolved in enough water to make 10 parts. One litre of this solution does not contain more than 100 grammes of protoxide of cobalt; therefore, 100 cubic centimetres will hold 10 grammes. This liquor is kept for use.

"If this solution be precipitated with the carbonate of soda, and if, after washing, the still wet precipitate of carbonate of protoxide of cobalt be mixed with zinc white, there is produced a reddish-violet magma, which, after being dried and calcined, constitutes a green mass, the color of which is the more intense in proportion as the cobalt solution has been greater.

"Cobalt green may be considered as a mixture of oxide of zinc and of zincate of protoxide of cobalt (corresponding with the aluminate of cobalt of the cobaltic ultramarine or Thénard blue). Ammonia dissolves the oxide of zinc first, and then the zinc cobaltic combination, from the calcined cobalt green. Melted glass is, of course, colored blue by this pigment. If the cobaltic solution be employed in such proportion that, for one equivalent of oxide of zinc, there be one equivalent, or more, of protoxide of cobalt, the calcined pigment will be a dirty green or a black. The best tone of this green is obtained by the combination of 9 to 10 parts of oxide of zinc, with 1 to 1.5 parts of protoxide of cobalt. But, in every case, this pigment never attains the brightness of copper greens, or even of ultramarine green.

"Mr. Louyet, a Belgian chemist, has shown, in a work on the preparation of oxide of cobalt and of aluminate of protoxide of cobalt in a pure state, that an addition of phosphoric or of arsenic acid enhances the beauty of the color. If the addition of these acids aids in the combination of protoxide of cobalt with alumina, it should also act favorably in the preparation of cobalt green. Experience has confirmed this inference. If the cobaltic solution be precipitated by the phosphate or the arseniate of potassa, the phosphate or the arseniate of cobalt thus produced possesses the property of imparting a green coloration to zinc white, at a temperature much lower than that necessary with the ordinary protoxide of cobalt. Moreover, the protoxide of cobalt seems to have gained more body. The green is also of a purer color and brighter. The alkaline arseniates act like phosphoric and arsenic acids. If before the calcination a small proportion of arsenious acid be added to the ordinary mixture, the calcined mass will be of an exceedingly bright green, and its structure being loosened by the volatilization of the arsenious acid, it will be easy to grind. I therefore call the attention of those who may desire to manufacture cobalt green, to this property of arsenious acid, by which the beauty of the color is considerably improved.

"Since boric (boracic) acid aids the combination of the protoxide of cobalt with the oxide of zinc, it may also possess an advantageous effect; but I have not yet discovered the best form in which it could be added to the mixture. The borate of protoxide of cobalt, added to a considerable proportion of zinc white, produces, after calcination, a bluish-green; with a smaller proportion of zinc, the mass is blue and compact.

"I have obtained an entirely similar result by precipitating a solution of protoxide of cobalt with soluble glass (silicate of soda or of potassa), mixing the silicate of cobalt with zinc white, and calcining.

"The oxide of antimony, which is isomorphous with arsenious acid, and which is obtained by the precipitation of the perchloride of antimony with carbonate of soda, has brought no change whatever in the color of the cobalt green."

Mr. R. Wagner has made analyses of Rinmann greens manufactured in Germany. A light green sample, from the technological cabinet of the University of Würzbourg, was composed of—

Oxide of zinc	88.040
Oxide of iron	0.298
Protoxide of cobalt	11.662
	100.000

Other kinds of green, prepared by himself a few years before, were finer than the best qualities of copper greens without arsenic. Their composition was—

	I.	II.
Oxide of zinc	71.93	71.68
Protoxide of cobalt	19.15	18.93
Phosphoric acid	8.22	8.29
Soda	0.69	

Messrs. Barruel and Leclaire prepare a Rinmann green, which they call zinc green, by the following process: 49 kilogrammes of dry and pure sulphate of cobalt are dissolved in hot water, and this solution is mixed with 245 kilogrammes of zinc oxide, prepared in the manner given in the paragraph on yellow chromate of zinc. The mixture is dried and then calcined at a clear red heat, for three hours, in a muffle. When the substance has cooled off a little, it is thrown into water, washed, and dried.

Messrs. Barruel and Leclaire have also discovered another zinc green, in which this metal is combined, not with cobalt, but with iron, and which appears to be a ferroso-zinc cyanide. The following is the mode of preparation. Prussian blue is finely powdered and stirred in a concentrated solution of chloride of zinc. This magma is put aside for some time, and, when it has acquired the desired hue it is thoroughly washed, and the precipitate is dried in the dark. This green is very handsome, but possesses but little durability.

§ 25. *Chrome green.*

Chrome green is the sesquioxide of chromium, which is prepared in the arts by several processes which we shall now describe.

1. The bichromate of potassa is calcined in a crucible, and is transformed into chrome green and potassa, the latter of which is washed out.

2. The bichromate of potassa is decomposed by hydrochloric acid, when there is formed a soluble chloride of potassium, and a green oxide of chromium.

3. A concentrated solution of bichromate of potassa is heated, and while boiling, sublimed sulphur is added to it by small quantities at a time. The mixture soon becomes greenish, and the chromic acid is transformed into a gelatinous oxide, which is washed with boiling water, dried, and calcined at a red heat in a crucible.

Or, by the dry way, an intimate mixture of equal parts of bichromate of potassa and of sublimed sulphur is brought to a red heat in a crucible. The product is treated by hot water, which dissolves the sulphide of potassium and the sulphate of potassa formed, and leaves the oxide of chromium in the state of a green powder, finely comminuted.

4. A solution of bichromate of potassa is poured into a neutral solution of proto-nitrate of mercury. There is formed an orange precipitate, which is washed, and dried at a gentle heat. It is then powdered, and heated in a stoneware retort, which is provided with an adapter dipping in cold water. The mercury distils, and is condensed in the water. The residue in the retort is a pulverulent oxide of chromium of a fine and dark green.

5. A mixture of 3 parts of neutral chromate of potassa and 2 of sal ammoniac, is heated in a crucible. The two salts are decomposed, and there is formed an oxide of chromium mixed with chloride of potassium. The latter salt is removed by several washings of hot water. A calcination at a dark-red heat increases the brightness of the product.

6. An intimate mixture of 1 part of bichromate of potassa, and 1 of potato starch (fecula), is calcined at a high temperature in a crucible. The product is washed with boiling water, in order to remove the carbonate of potassa formed, and a small proportion of undecomposed bichromate. The precipitated oxide is filtered, dried, and calcined again to remove the water. It is said that this oxide is of a very handsome color, and that it is easily applied with the brush.

Mr. F. Casoria, an Italian chemist, being desirous of ascertaining the comparative value of the first four processes, made his experiments especially in view of establishing the gradation of color of the same oxide.

"1. The first process, says he, which I have tried twice, and which is based upon the decomposition of chromate of mercury, gave me a very comminuted material, of a dark-green color.

"2. The sesquioxide of chromium, precipitated from a solution of chloride of chromium by ammonia, is a green between a gray and a blue.

"3. The oxide of chromium, resulting from the decomposition of the bichromate of potassa alone, at a very high heat, is of a dark-green color and very compact. Its hue resembles that of the oxide obtained by the calcination of the chromate of mercury.

"4. Lastly, the decomposition of the bichromate of potassa by sulphur, has furnished a dense oxide of an intense green color.

"For my own satisfaction I have tried other processes, which gave me less satisfactory results."

§ 26. *Emerald green.*

Emerald green is another sesquioxide of chromium, prepared in a particular manner.

There has been in the trade for a long time, under the names of emerald green and Pannetier green, a handsome and durable color which was sold at a high price. The inventor, Mr. Pannetier, has not published his process, but communicated it to Mr. Binet alone, as an acknowledgment of the aid given by the latter person, in putting his pottery kilns at his disposal. All that is known of this secret composition, is that the green is a chromium compound, prepared in the dry way. A few experimenters have also said that they had found boric (boracic) acid in it.

The remarkable researches of Ebelmen upon the artificial production of mineral compounds have shown the advantages which may be had from boric acid as a solvent. At a high temperature, boric acid acts like a solvent, water for instance, and forms combinations more or less stable with the dissolved substance. The latter may be separated from the boric acid, either by a higher temperature, which volatilizes the acid, or by solution in water, alcohol, etc.

Ebelmen, when using boracic acid, employed the method of volatilization. Mr. Guignet uses it also as a flux; but, instead of removing it by a high temperature, he dissolves it in water. The following is a *résumé* of the mode of operation of Mr. Guignet.

This color may be prepared by two processes:—

First process.—There is heated, upon the bed of a reverberatory furnace brought to a dark-red heat, a mixture of 1 part of bichromate of potassa and 3 parts of boric acid, moistened with enough water to make a thick paste.* The product, while red hot, is thrown into cold water, and washed with boiling water, in order to remove the borate of potassa. The hydrated oxide of chlorium is dried or kept in the pasty state. By evaporating the liquors, and adding hydrochloric acid, the greater part of the boracic acid is recovered.

Second process.—The bichromate of potassa of the first process is replaced by an equal quantity of chromate of soda, which is prepared by dissolving in boiling water 61 parts of neutral chromate of potassa, and 53 parts of nitrate of soda. The neutral chromate of potassa may also be replaced by a mixture of 92 parts of bichromate of potassa, and 89 parts of crystallized carbonate of soda, and the indicated proportion of

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* The temperature should not be above a dark-red heat, otherwise the substance will fuse entirely, instead of forming a porous mass. The oxide will become anhydrous, the color of which is a pale green.

nitrate of soda remains as before. In either case, the solution, in cooling, deposits a quantity of nitrate of potassa (saltpetre), which pays one part of the expenses. The mother liquors contain the chromate of soda, which may be crystallized; or, what is preferable in this case, the liquors are evaporated to dryness, and the residue will be a sufficiently pure chromate of soda, provided all the nitrate of potassa has been separated.

By the second process of preparation of the chromate of soda, the indicated proportions give twice as much of chromate of soda as in the former case.

When the green color is manufactured with the chromate of soda, the liquors contain borax, which may be sold directly as such or converted into boric acid by the addition of hydrochloric acid. The color prepared from the chromate of soda is of a lighter green than that produced by the bichromate of potassa. Still lighter colored pigments may be obtained by adding to the mixture of bichromate and of boric acid, before calcination, a certain proportion of alumina, magnesia, blanc fixe, etc.

The chromates of potassa or soda may also be replaced by the chromate of lime, obtained by the direct calcination of chromic iron and chalk, in an oxidizing flame.

"Although the first process appears very simple, it is however necessary, says Mr. Casoria, to indicate a few precautions, which, if they were neglected, would result in an inferior product. The first condition is to avoid an excess of heat, and the best temperature is that below a red heat. If it be attempted to decompose entirely the bichromate of potassa by an increase of temperature, the colored precipitate will be abundant, but of a dirty green. The very large proportion of boracic acid has a manifest influence on the color of the oxide, as I have repeatedly ascertained by direct experiments."

In regard to the economy of the process, we should notice that the first washings deposit, in cooling, a large proportion of boric acid, and contain a certain proportion of borate of potassa and of undecomposed bichromate of potassa. It is not necessary to demonstrate that these two residua of the process may be used quite *ad infinitum* in the subsequent operations. Thus it is that a certain quantity of boric acid is sufficient for many operations.

This process may be tried with a very small quantity of materials, in a platinum dish, and over an alcohol lamp. The calcined substance, thrown into boiling water, deposits a green precipitate, which may be mistaken for the finest quality of Scheele's green.

Mr. Arnaudon has proposed in the *Technologiste*, vol. xx. p. 519, a different process for the preparation of an oxide of chromium, equal in color to the finest Schweinfurt green. The following is his process:—

Take the equivalent weights of the following salts:—

Neutral phosphate of ammonia (crystallized)	128 parts
Bichromate of potassa	149 "

and mix them thoroughly, either by grinding, or by dissolving them in a minimum of hot water, and exaporating the solution to the consistency of a magma, which becomes hard by cooling. This mass is broken into small pieces, which are heated in a shallow dish at the temperature of 170° to 180° C.

At that temperature the mixture becomes soft, then pasty, and soon intumesces, changes its color, and disengages a small proportion of water and ammonia. The heat is continued for about half an hour, without going above 200° C. Beyond that point, for instance at the temperature necessary for the production of Guignet's emerald green, the green coloration of the mixture disappears, and is replaced by a dark brown color due to binoxide of chromium. By raising the temperature still higher, at a brown-red heat for instance, the former color changes to a blue, which is durable in presence of water. If the temperature be maintained at that point, when the mixture has become green, and if the product be washed with hot water, to remove the soluble salts, there will be obtained a nearly impalpable powder of oxide of chrome, the color of which resembles that of new leaves, and forms a near approach to the green of the first chromatic circle of Mr. Chevreul.

The green obtained by this process, freed from soluble salts by washings in hot water, dried at 160° C., and brought to a red heat in a tube, gives off water, and does not become dark like the bihydrate of MM. Guignet and Salvetat. While hot, it is of a violet-red color, which passes to a gray,* and, lastly, to a green when entirely cold. However, the hue is different from that presented by the green before its calcination; and by operating with care, a green of anhydrous sesquioxide of chromium may be obtained, which rivals that of Schweinfurt. Mr. Arnaudon is not positive in regard to the composition of this green, because, notwithstanding repeated washings,

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* This gray coloration is due to less red and more green, which complementary colors, by their combination, produce black.

it will still show the presence of phosphoric acid after a fusion with a mixture of nitrate and carbonate of potassa. The proportions obtained do not allow of a certain decision as to whether this acid is combined in definite proportions, or simply held by what Mr. Chevreul calls capillary affinity; that is to say, by an affinity analogous to that of tannin for leather, or of coloring substances for tissues.

Mr. Arnaudon, disregarding the fact of the traces of phosphoric acid obtained, has found that this sesquioxide of chromium contains about 11.70 per cent. of water, which corresponds to the monohydrate of sesquioxide of chromium $Cr^2O^3.HO$.

This chrome green is remarkable for its property of preserving its brightness and purity under artificial light. It resists acids, alkalies, and sulphuretted hydrogen. The colors resulting from its mixture with other pigments are not altered, and it is not poisonous. On account of all these advantages, it is to be desired that painters should employ it in their works. Indeed, if their pallets were entirely composed of colors as durable as this one, their chefs d'œuvre would pass unaltered through ages, and with less danger of being disfigured by unskilful restorations.

This pigment may also be used for calico-printing with albumen, etc.

§ 27. *Titanium green.*

Mr. L. Elsner has proposed to prepare with titanium a green color without arsenic or copper. The following is the process described by this chemist:—

Several years ago, says Mr. Elsner, Lampadius had published a few experiments he made for the purpose of preparing a dark green color from rutile.* He melted at a red heat, in a Hessian crucible, 500 parts of powdered rutile, and 1500 parts of purified potassa. The melted mass was saturated with hydrochloric acid, then filtered, and the clear liquor was precipitated with a solution of ferrocyanide of potassium. The precipitate, washed and dried, was titanium green. With 500 parts of rutile, Lampadius obtained 855 parts of green. The preparation of titanium green, either from washed rutile or iserine, has been found more advantageous by the following process:—

The clean ore is melted with twelve times its weight of acid sulphate of potassa in a Hessian crucible. After cooling, the melted mass is powdered, and digested until it is dissolved in hydrochloric acid diluted with 50 per cent. of water, maintained at the temperature of 50° C. The hot solution is separated from the insoluble residue by filtration, and the filtrate is evaporated until a drop of the liquor, put upon a piece of glass or porcelain, becomes of the consistency of a magma. The whole is allowed to cool off in the porcelain dish, and the magma, composed of nearly pure titanic acid, is thrown upon a filter. The drainings are again evaporated, and furnish a new portion of titanic acid. When the magma has been sufficiently drained, it is mixed with a large volume of water, holding a small proportion of ammonia, in order to prevent the formation of a basic salt of iron. This liquor is kept boiling for a long time, and the

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* Rutile is titanic acid mixed with a greater or less proportion of the oxides of iron and manganese, and sometimes of oxide of chromium. Iserine or nigrine is a combination of titanic acid with oxide of iron, and a few other substances.

precipitated titanic acid, after filtration and washings, is nearly white. After several similar treatments with the bisulphate of potassa, it may be obtained entirely free from iron.

As iserine contains generally some carbonate of lime, it is advisable to digest it with dilute hydrochloric acid, before it is treated with the acid sulphate of potassa.

A concentrated solution of sal ammoniac is poured upon the magma, prepared in the manner explained above, and, after a thorough mixing, it is filtered. The titanic acid remaining upon the filter is digested in diluted hydrochloric acid, and kept at a temperature of 50° to 60° C., until the solution is as complete as practicable. The acid liquor, after the addition of ferrocyanide of potassium, is rapidly brought to a boil, and there is formed a precipitate of a handsome titanium green, which is washed with water holding a small proportion of hydrochloric acid. The solution of titanic acid must be very acid, because if pure water be employed, and the ferrocyanide poured upon the magma, the precipitate will be a yellowish-brown becoming green by ebullition in dilute hydrochloric acid. The green precipitate becomes white with ammonia. The liquor, filtered from the green precipitate, still contains a certain quantity of titanic acid, which ammonia will separate in the shape of a white flocculent precipitate.

The dry titanium green, obtained either from rutile or iserine, is a dark-green powder. It is decomposed at the temperature of 100° C. Its desiccation should therefore be carefully conducted.

By this method, iserine and any titaniferous iron-ore will produce a green as handsome as that prepared from rutile. Moreover, the liquor holding the double sulphate of iron and potassa will give a Prussian blue by the addition of ferrocyanide of potassium. Therefore, this method will allow of the manufacture, with iserine, of titanic acid, titanium green, and Prussian blue.

§ 28. *Green ochre.*

Mr. Bouland, of Orleans, has composed a color, called green ochre, by the following formula: 50 kilogrammes of dry ochre, in powder, are mixed into a paste with water and 1 kilogramme of hydrochloric acid. Twenty-four hours after, 1 kilogramme of yellow prussiate of potassa is also thoroughly mixed with the above paste. Lastly, an aqueous solution of persulphate of iron is added in order to arrive at a given hue.

A great variety of hues may be obtained by changing the proportions of yellow prussiate. This green is used in the manufacture of paper-hangings.

§ 29. *Green ultramarine.*

This is a light bluish-green, having a composition similar to that of blue ultramarine; that is, it contains sulphur, silica, alumina, soda, with traces of iron and lime. The difference appears to be a greater proportion of sulphur in the green ultramarine. Indeed, with the same temperature, if air be allowed to come in contact with the crucibles containing the ultramarine, this substance will be blue. On the other hand, if air does not intervene for burning the excess of sulphur, the ultramarine will be green, but will pass to a blue by a calcination in the air.

Green ultramarine possesses a certain brightness under artificial light, resists sulphuretted hydrogen, and is not readily attacked by alkalies; but the weakest acids decompose it with production of sulphuretted hydrogen. Mixed with other colors, or ground with oils, gums, or varnishes, it is altered if these substances be acid, or will develop acidity.

§ 30. *Verdigris.*

Recent researches have shown that verdigris is a basic hydrated acetate of copper, composed of variable proportions of bibasic and tribasic acetates of copper. We shall not tarry on the manufacture of this color, which was known to the painters of antiquity, and which forms a special trade in certain localities.

Verdigris is manufactured in France, in the departments of Aude and Hérault, by oxidizing pieces of old sheet copper from 2 to 3 millimetres thick, heated to 80° C., with a solution of acetate of copper, and then immersing them in the skins of pressed grapes, which are in a state of acetic fermentation. After a certain length of time, which is indicated by experience and various phenomena, the copper plates are removed from the skins, dried in the air, then dipped into water, and again laid in layers of grape skins. When this operation has been repeated five, six, or seven times, the verdigris has acquired a thickness of from 2 to 3 millimetres, and is scraped off, then kneaded in wooden troughs, and packed in leather bags. Its desiccation is completed in the air.

Verdigris is also prepared by covering copper plates with vinegar.

Verdigris is of a pure green, or of a bluish-green, according to the proportion of sesquibasic acetate it contains. When it is pure it is entirely dissolved, and without effervescence, in diluted nitric and sulphuric acids. It is highly poisonous, and is not a durable color.

§ 31. *Crystallized verdet. Distilled green. Crystals of Venus.*

Verdet is a neutral acetate of copper which is manufactured in the south of France. This salt is of a fine green color, its taste is sweet and styptic at the same time, and it is soluble in water and alcohol. Its crystals form very regular rhombs, of a very dark green. It is decomposed by heat, and the distilled acid produced is colored by a small quantity of oxide carried away mechanically. According to Vogel, a small proportion of anhydrous acid is sublimed at the same time in the shape of white silky crystals.

This acetate of copper is prepared by dissolving verdigris in vinegar, filtering the solution, and letting it crystallize.

This salt is employed for water-color painting. It is very poisonous, and the green coating deposited upon copper vessels is still more dangerous.

The verdet may be obtained by double decomposition, and, indeed, this is the process generally followed in the factories where acetic acid is prepared from distilled wood. A solution of 100 kilogrammes of acetate of lime is decomposed by one of 140 kilogrammes of sulphate of copper; there results an insoluble sulphate of lime, and a solution of acetate of copper, which is decanted, evaporated, and crystallized.

The liquor known under the name of *water-green*, and used as a water-color, is prepared by dissolving the most colored crystals of verdet in a slightly alkaline water.

SECTION VII.

COLORS FROM SULPHATE OF ZINC.

We shall close our remarks on colors by describing a process for the preparation of colors with the oxide of zinc, which has been proposed by Messrs. L. Ador & E. Abadie.

"The oxide of zinc, which forms the basis of this manufacture, is obtained by the decomposition of the salts of this metal by heat, either in furnaces or in retorts. The advantage of these colors is their salubrity and their economy. When the oxide derives from decomposed sulphates, monohydrated sulphuric (Nordhausen) acid is disengaged, and the remaining oxide, by its combination with other metallic oxides, forms all the colors, hues, and tones which may be desired.

"The sulphate of zinc is prepared as follows: Metallic zinc is dissolved in sulphuric acid marking 18° to 20° Bé. When the saturation is complete, the liquor is left to stand until it is clear, and it marks then 36° to 38° Bé. The liquor is then evaporated in leaden vessels until it forms a pasty mass, which is spread and cooled upon zinc or lead plates. The salt is broken as finely as practicable with a wooden spatula.

"The mixtures of metallic salts forming with sulphate of zinc various colors, are as follows:—

"*Delicate light yellows*, called *Roman yellows.*—They are obtained by a simple decomposition by heat of the sulphate of zinc in retorts and in furnaces.

"*Chamois yellows.*—100 parts of sulphate of zinc in solution, are mixed with 1¼ parts of a solution of sulphate of iron marking 28° to 30° Bé.

"*Yellow chamois.*—100 parts of sulphate of zinc in solution, are mixed with 2½ parts of a solution of sulphate of iron marking from 28° to 30° Bé.

"*Dark chamois.*—The proportion of iron solution is increased to suit the hue desired.

"*Gold yellows.*—100 parts of sulphate of zinc in solution are mixed with 2½ parts of a solution of nitrate of manganese marking 12° to 14° Bé.

"*Dark gold yellows.*—The proportion of nitrate of manganese is increased to suit.

"*Greens resembling Scheele's greens.*—100 parts of sulphate of zinc, in solution, are mixed with 2½ parts of a solution of nitrate of cobalt marking 20° Bé.

"*Dark greens.*—The proportion of nitrate of cobalt is increased.

"*Yellowish greens.*—100 parts of sulphate of zinc are mixed with 2½ parts of a solution of nitrate of nickel, at 16° Bé., and a few drops of a solution of nitrate of silver.

"*Grays.*—100 parts of sulphate of zinc in solution, are mixed with 2½ parts of a solution of sulphate of copper.

"*Bronzes.*—100 parts of sulphate of zinc are mixed with 3 parts of a solution of nitrate of nickel at 15° to 16° Bé., 3 parts of a solution of nitrate of cobalt of the same specific gravity, and from 1 to 1½ per cent. of a solution of nitrate of copper of the same specific gravity.

"*Dark bronzes.*—The same materials are employed, in the same proportions, but they are calcined longer.

"*Pinks.*—100 parts of sulphate of zinc in solution, are mixed with 2 to 3 parts of a solution of nitrate of iron marking 20° to 25° Bé.

"*Dark pinks.*—The proportion of nitrate of iron is increased.

"*Whites.*—They are obtained by employing a sulphate of zinc very pure, especially free from iron, which is tested with the sulphocyanide of potassium. The greatest care should be taken to employ clean drying vessels, and the cooling of the sulphate should be made in stoneware pots.

"The various combinations of materials, and the chemical reactions which produce these colors, require a variable length of time for the transformations to be completed, according to the apparatus employed, the temperature, and the colors or hues desired. The operation requires to be watched attentively, and the fire should be removed as soon as the given hue or tone is obtained.

"The sulphate of zinc, mixed with the other solutions of coloring oxides, is reduced to a thick paste, which is introduced into a furnace or into a retort. The calcination lasts from four to eight hours in retorts, and about one-half of this time in reverberatory furnaces. Side openings allow of the watching of the operation in the furnace, and of the extraction of the materials when the desired hue has been obtained.

"The colored oxides of zinc, after their removal from the retorts or furnaces, are pulverized in conical mills or under stones, and then more finely ground and sifted.

"The nitrates, chlorides, and acetates of zinc produce similar results when they are treated in the same manner with the same metallic salts. Every kind of color may also be prepared by calcining carbonate of zinc with the carbonates of the coloring metals; but, instead of working them by the wet way, they are employed in powder and treated by the dry method. It is necessary that the carbonates of zinc, iron, copper, cobalt, antimony, manganese, bismuth, nickel, etc., should be very pure.

"The proportion of the coloring carbonates should not be less than 6 per cent. of the weight of the carbonate of zinc, and the amount is increased according to the hue desired.

"The operation requires two or three hours of calcination. When the color and the hue have been obtained, the substances are removed from the furnace, ground, and sifted in the afore-mentioned manner."

CHAPTER III.

DRYING AND ADHERENCE OF COLORS.

A VERY important question in applying colors is the facility with which they dry, when they have been ground with water, essential or fixed oils, or varnishes. Indeed, it is necessary that these paints should rapidly acquire a certain degree of desiccation in order that the places where they have been applied may be inhabited, and also for the purpose of rendering them resisting to friction. Until recently, colors were made drying by the single process of mixing them with oil boiled with litharge; but chemistry has caused improvements to be introduced into this part of the painter's art, on which it will be useful for us to tarry a little while.

SECTION I.

DRYER FOR ZINC WHITE.

The colors prepared with zinc white dry more slowly than those of white lead. Mr. Leclaire has therefore searched for a dryer more powerful than litharge, and has ascertained that the peroxide of manganese is preferable to all the other metallic oxides. The following is his process:—

Purified linseed oil is boiled for 6 or 8 hours, and to every 100 kilogrammes of boiled oil there are added 5 kilogrammes of powdered peroxide of manganese, which may be kept in a bag, like litharge. The liquid is boiled and stirred for 5 or 6 hours more, and then cooled and filtered.

This drying oil is employed in the proportion of 5 to 10 per cent. of the weight of zinc white, and it is better to add it during the grinding of the pigment in oil, since the mixture is more thorough.

SECTION II.

DRYING OILS.

Mr. Leclaire has not confined himself to the above process for oxidizing oils, but he has also searched for a mode of rendering them thicker, and indicates the following method:—

Oil oxygenized (oxidized) by the peroxide of manganese, says he, may be thickened to the point of becoming solid, when it will produce the same effects as litharge.

Fifteen parts of lime, made into paste with water, are added to 100 parts of oil oxidized by the peroxide of manganese. The whole is boiled, or heated by steam, until the water has evaporated; the oil forms then with lime a thick product which is a dryer. It is sold in lumps, or in powder, or ground with an equal weight of oxidized oil. It may be ground with the ordinary essence of turpentine, or with that of Venice, but the dryer is less powerful than when it has been mixed with oxidized linseed oil. Three to five per cent. of this dryer are sufficient for a rapid desiccation.

Other dryers may be made by combining lime with resins and essences of turpentine, in the proportions indicated for fixed oils.

SECTION III.

POWDERED DRYER OF GUYNEMER.

For a long time, says Mr. Guynemer in a patent taken out for this purpose, it has been a desideratum to find an impalpable white powder which may be intimately incorporated with zinc white, and which will accelerate its desiccation.

The use of litharge and acetate of lead, as dryers, is open to the inconvenience of diminishing the unalterability and innocuity of zinc white; and on this account, Mr. Leclaire has proposed for zinc white an oil rendered drying by manganese.

The employment of these oils is sometimes difficult, because their preparation is not well understood everywhere, and because the expenses of transportation, the leakage, and the duties are heavy. It happens, also, in certain cases, that the brightness of the pigment is impaired.

Mr. Leclaire, in his patents, claims the mode of rendering oils drying, and the use of all the combinations of manganese as dryers.

The Society of the Vieille-Montagne, represented by Mr. Guynemer, has become the owner of the patents of Mr. Leclaire, and the following formula is a new manganese dryer, in powder:—

Take—Pure sulphate of manganese	1 part
Pure acetate of manganese	1 "
Calcined sulphate of zinc	1 "
White oxide of zinc	97 parts.
	100

The sulphates and the acetate are ground in a mortar to an impalpable powder, which is passed through a metallic sieve.

Three parts of this powder are dusted over the 97 parts of oxide of zinc, spread over a board or a slab. The whole is then thoroughly mixed and ground.

The resulting white and impalpable powder, mixed in the proportion of ½ to 1 per cent. with zinc white, will enormously increase the drying property of this product, which will become dry in 10 to 12 hours.

SECTION IV.

VARIOUS DRYERS. ZUMATIC DRYER.

Mr. Zienkowicz is the chemist who appears to us, in a patent described Vol. xxiv. p. 319 of the *Recueil des Brevets d'Invention*, to have investigated the question of dryers for painting the most thoroughly.

We reproduce here an extract from this work on the preparation of the zumatic dryer.

"Since it has been tried to substitute zinc oxide for white lead in painting, it is natural that researches should also have been made to replace litharge, as a dryer, by a substance free from the inconveniences which caused the abandonment of white lead. Indeed, if sulphuretted hydrogen impairs the whiteness of the painting done with white lead, it is not logical to employ a lead dryer with zinc paints, because the latter substances will lose their advantages of not becoming dark like white lead.

"It has been known for a long time, that several metallic oxides and salts, especially the sulphate of zinc, umber, and the oxide of manganese, have the property of combining with oils, which they render drying. But oxide of lead having been found to possess the greatest action upon oils, it has been preferred to the others, up to the present time, since its employment in connection with white lead does not present the same inconvenience as with zinc white.

"To the afore-named oxides, we should add the protoxides of the metals of the third class (Thénard's chemistry), that is to say, those of iron, cobalt, and tin. However, as the greater number of these protoxides are either difficult to prepare, or rapidly altered in the air, they cannot be kept and employed in practical operations. We have therefore searched out as to whether these oxides, combined with certain bodies, could not be manufactured in an economical manner, and could not preserve their drying action upon oils, from the time that they are prepared, to that when they are employed.

"Moreover, it is acknowledged, that dryers in the dry state are preferable in many respects to drying oils. But the difficulty lies in their proper preparation.

"The preceding considerations caused me to search for a process for producing the drying of the oil employed with zinc white, without litharge or any oxide of lead. A similar result has been arrived at by other persons with more or less success.

"I have therefore availed myself of the indications furnished by various authors upon the choice of certain materials, while, on the other hand, I have made original researches and experiments based upon a theory which it is not necessary to explain in this place.

"However, I should say that one of the principal bases of my process is founded upon the combination of the protoxides of the metals of the third class (Thénard's chemistry), that is, those of iron, tin, nickel, manganese, and cobalt, with benzoic, succinic, urobenzoic, and boric acids, which, at the same time that they preserve these oxides from the oxygen of the air, do not prevent them from acting upon the oils as a ferment, which causes the absorption of the oxygen of the air by these oils, and their resinification or drying. Any acid, combined with these protoxides, with sufficient affinity to render the manufacture of such dryers easy and economical, and to preserve them, is comprised in my processes. At the same time, the affinity of the acid for the protoxide should not be so strong as to prevent the latter from acting upon the oils. Carbonic acid is disengaged by the action of the air in contact with the oils mixed with these dryers.

"I could include within these claims the above-mentioned protoxides, although they have been indicated before me; but it is impossible to employ them in the manner specified by the authors, especially the pure protoxide of manganese.

"The various experiments which I have made up to this date, prove that the preference should be given to the urobenzoate and to the borate of cobalt; but economical considerations favor the employment of the urobenzoate and the borate of manganese.

"I shall now explain the processes of preparation and of manufacture, which I have followed.

1. *Benzoate of Cobalt, and Benzoate of Manganese.*

"Benzoic acid is dissolved in boiling water, and the stirred liquor is gradually saturated with powdered carbonate of cobalt, until all effervescence ceases, and blue litmus paper does not turn red in the liquor.

"The excess of carbonate is separated by filtration, the liquor is evaporated to dryness, and the heating is continued until the salt has lost all its water, and has become of a light brown color. The salt thus prepared is an amorphous, hard, and brownish material, which may be powdered like rosin, and which may be kept in the pulverulent state, in any climate, simply folded in paper.

"An experiment made by me with this drying salt has proven that, in the proportion of 3 kilogrammes to 1000 kilogrammes of linseed oil, mixed with about 1200 kilogrammes of zinc white, a piece of painting was dried in from eighteen to twenty hours. The temperature was relatively cold and wet, and between 12° and 15° C.

"The benzoate of manganese is prepared in the same manner, by substituting the carbonate of manganese for that of cobalt. The manganese dryer presents nearly the same physical characteristics as the cobalt salt. Applied under the same conditions, it dries a little more rapidly, and a little less is needed.

"The high price of benzoic acid induced me to search for a congenerate of this acid, which would form saline combinations having the same properties, and which would be cheaper.

"I have, therefore, tried the urobenzoic (hippuric) acid, which my experiments have proven as efficacious. The urobenzoates of cobalt and of manganese are obtained in the same manner as the benzoates of these bases.

"The materials which I have experimented upon are relatively too expensive for industrial uses; but there is every hope that it will be possible to obtain the benzoic and urobenzoic acids in an economical manner.

2. *Borate of Cobalt.*

"A soluble salt of cobalt, the sulphate for instance, is dissolved in cold water, and this solution is precipitated by a cold one of borax (biborate of soda). The precipitate of borate of cobalt is collected upon cloth filters, washed with cold water, and dried in the air.

"The borate of manganese is prepared in the same manner by substituting for the cobalt salt a soluble one of manganese, the chloride for instance, which is cheap.

"These borates are kept and used in the same manner as the preceding dryers.

3. *Employment of Resins.*

"With the same view, that of preparing a dryer in the dry state, free from any foreign substance which might impair its drying properties and render it hygrometric, I have tried the employment of resins, which, from their acidity, play a part analogous to that of the acids already mentioned.

"Thus, by applying to cobalt and manganese the process hereinafter described, I have obtained a real drying salt, containing no substance not in harmony with the effect to be produced, and which may be kept in the pulverulent state as the afore-mentioned drying salt.

"An alkaline resinate of potassa or soda is dissolved in hot water, and this solution is precipitated by a suitable proportion of the pure sulphates or chlorides of cobalt or manganese. The precipitate thus formed is a resinate of cobalt or manganese, which is collected upon cloth filters, washed, and dried.

"These resinates are amorphous, and are powdered and kept in the same manner as the other dryers. They possess the same properties, and are employed under the same conditions and in the same proportions.

4. *Borate of Manganese.*

"In continuing my investigations, especially on the employment of the borate of manganese, I remarked that the protoxide of manganese absorbed the oxygen of the air with great rapidity, passed to the intermediary degree of oxidization, and at the same time separated from the acid with which it was combined. I found, also, that if more than 2 or 3 parts of this manganese salt per 1000 parts of zinc white were added, the paint, especially the white grounds, would acquire a prejudicial coloration.

"In order, therefore, to remedy this inconvenience, which may often take place from carelessness in compounding the proportions, I have been obliged to find a method for neutralizing the troublesome effects of an excess of dryer in the paint.

"I mix in advance the borate of manganese with a certain proportion of oxide of zinc, and, in this diluted state, the proportion of dryer with the zinc white paint may be in excess with less danger. I will however remark that this arrangement does not entirely do away with the necessity of making the proper mixtures, but that it allows of a certain amount of carelessness or ignorance in the compounding of the paints.

"The following is the manner of mixing the dryer with a certain proportion of zinc white, and how this mixture is to be added to the white pigment and oil, before painting:—

"A thick aqueous magma of 30 grammes of borate of manganese is thoroughly mixed with 1 kilogramme of recently prepared oxide of zinc, of the first quality, and made into a thin paste with water. The mixture is drained upon a cloth, then pressed and dried in a stove room. It is kept in a pulverulent state, in barrels, or in paper sacks.

"This proportion of dryer, added to 20 kilogrammes of zinc white, will be sufficient to dry the paint rapidly; and should the proportion of zinc white be reduced one-fourth or one-fifth, or that of the dryer increased in the same proportion, the color of the paint will not be altered.

"The borate of manganese as a dryer is so energetic that it is proper to reduce its action in the following manner:—

"One kilogramme of borate of manganese is powdered and mixed with 25 kilogrammes of zinc white, first with the hands, and then in a revolving drum.

"In decoration and artistic painting, dryers, whatever they be, are employed only with bitumens and lakes, for glazing, that is to say, for transparent coats.

The zumatic dryer cannot conveniently be used for such purposes, on account of the opacity and body of the zinc white entering into its composition. I have therefore replaced the oxide of zinc by a substance which answers the same object as alumina in lakes, that is, a material without opacity, and affecting in no way the color and the transparency of the paints with which the dryer is mixed.

"The substance employed for such an admixture with the borate of manganese, or with the other salts already mentioned, is the pure carbonate of zinc, obtained by the precipitation of a soluble zinc salt by an excess of a solution of crystallized carbonate of soda.

"The carbonate of zinc may be replaced by the sulphate of baryta, clay, the carbonates of lime or magnesia; in fact, by any substance which becomes translucent in oil. But it is preferable to employ the carbonate of zinc, which adds to the value of the new article, and cannot be considered as an adulteration.

"This new product has been called *zumatic lake.* It is prepared according to the following formula, which contains about as much borate of manganese as the zumatic dryer:—

Carbonate of zinc	90 parts in weight.
Borate of manganese . . .	10 "
Linseed oil	90 "

"The whole is most thoroughly ground, and kept in bladders or in tin tubes. The latter are preferable.

"Since the borate of protoxide of manganese causes also the rapid drying of the oils employed in the preparation of inks for typography, lithographic and copperplate printing, Messrs. Barruel & Jean have recommended the use of borate of manganese in the manufacture or the employment of printing inks.

"The use of the borate of protoxide of manganese may still be extended to the preparation or the employment of fixed oil varnishes, since they acquire a great tendency to dry without loss of brightness or tenacity.

"Lastly, the borate of manganese may be very advantageously employed in the preparation of patent leather and oil cloths."

SECTION V.

SPREADING, DRYING, AND ADHERING PROPERTIES OF OIL PAINTS.

Mr. Chevreul published in the *Annales de Physique et de Chimie*, 1857, a very important memoir on oil painting, which is a real treatise on that art. We should have liked to have entirely reproduced this work of the illustrious chemist, but it is too extensive for this volume. We shall therefore confine ourselves to a *résumé* and the conclusions of the author as follows:—

"Painting is done with two objects in view, either to change the natural color of the surfaces of various articles, or to protect those articles by rendering their surfaces less easily altered by air, rain, dust, etc.

"Three conditions must be fulfilled:—

"*First.* The paint must possess sufficient fluidity to spread with the brush, and also be viscous enough to adhere to the surfaces without running, and to leave coats of equal thickness, when the surfaces are inclined, or even vertical.

"*Second.* The applied paint must become hard.

"*Third.* After it has become hard, it must adhere strongly to the surface upon which it has been applied.

"I have proved that the hardening of white lead or zinc white paints, is due to the absorption of the oxygen of the atmospheric air. And since pure oil hardens, we see that the hardening is the effect of a primary cause, which is independent of the dryer, white lead, or zinc white.

"Besides, my experiments demonstrate that white lead and oxide of zinc manifest a drying property in many cases, and that this property exists also in certain substances which are painted—lead, for instance.

"Therefore, the painter desirous to know, at least approximately, the length of time necessary for his painting to become dry, will have to consider all the causes which produce that effect. Consequently, a *dryer* will not be considered as the *only cause* of the drying phenomenon, since this phenomenon is assisted by several substances, having also the property of drying under certain circumstances. Moreover, there is this remarkable fact, that the *resultante* or sum of the activities (drying powers) of each of the substances entering into the composition of the paint, cannot be reckoned by the sum of the activities of each substance. Thus, pure linseed oil, the activity (drying power) of which is represented by 1.985, and oil treated by manganese with an activity of 4.719, will, when mixed, possess an activity of 30.828.

"If there be substances increasing the drying property of pure linseed oil, there are others which seem to act in the opposite direction. For instance:—

"Linseed oil, with one coat applied upon glass, was dry after 17 days.

"The same oil, mixed with oxide of antimony, took

26 days to dry. In this case, the oxide of antimony was an *anti-dryer.*

"Linseed oil, mixed with oxide of antimony, and applied upon a cloth painted with white lead, was dry after 14 days.

"The same oil, mixed with the arseniate of protoxide of tin, and applied upon the same cloth, was not hard after 60 days.

"Oak wood appears to possess the anti-drying property to a high degree, since, in the experiment of December 22, 1849, three coats of oil took 159 days to dry.

"In the experiment of May 10th, 1850, a first coat of linseed oil was dry, only on the surface, after 32 days.

"Poplar seems to be less anti-drying than oak, and Norway fir, less than poplar.

"In the experiment of May 10th, 1850, three coats of linseed oil took to dry: 27 days for poplar wood, and 23 days for Norway fir.

"If there be a drying activity, and a contrary one, in certain substances, I have no doubt that there are also circumstances, under which linseed oil is not influenced by the nature of the surface upon which it has been spread. For instance, in the experiences of May 10th, 1850, one coat of linseed oil was given upon surfaces of copper, brass, zinc, iron, porcelain, and glass; and in every case the oil was dry after 48 hours.

"I hasten to say that I do not pretend to classify all the substances in contact with linseed oil, or any other drying oil, into drying, anti-drying, and neutral or indifferent, because the circumstances under which these substances are placed may cause variations in their properties. I believe that a substance may be drying, or anti-drying, under different circumstances, whether it be due to the temperature, or to the presence or absence of another substance, etc. For instance, metallic lead is drying towards pure linseed oil; whereas, white lead, which is well known as possessing drying properties, is anti-drying towards linseed oil applied upon metallic lead.

"If painters desire to understand their operations well they must consider the drying of their painting in the same manner as I have just pointed out. By so doing, and in certain determined cases differing one from the others, they will be enabled to modify and improve their ordinary methods. Linseed oil is naturally drying, and this property increases almost always by its admixture with white lead, and in certain cases, with oxide of zinc. If the mixture be not sufficiently drying, recourse is to be had to an addition of oil boiled with litharge or manganese. At the same time it is necessary to consider the nature of the surface painted over, whether it be a first, second, or third coat, the temperature of the air, the light, etc.

"From our present point of view, drying oil boiled with litharge or manganese loses part of its importance, because it may be dispensed with for the second and third coats, and even for the first one if the natural drying is aided by the temperature.

"Moreover, pigments themselves may act as substitutes for it, as in the case of light colors, which are altered by yellows or browns, if the painter has derived profit from some of the observations indicated in this memoir.

"Thus, linseed oil, exposed to the air and to light, becomes drying, and loses its color; it may therefore be employed with white lead or zinc white, without impairing the whiteness of either.

"Since by associating oxide of zinc with carbonate of zinc, it is possible to dispense with a dryer, we have a new way of avoiding the inconveniences of colored dryers. At the same time, it gives a hope that new combinations of colorless substances will be found presenting greater advantages than those just noticed.

"My experiments demonstrate that the processes generally followed by color manufacturers, for rendering oils drying, that is, by heating them with metallic oxides, are open to the objections of waste of fuel and coloration of the product. Indeed, I have shown—

"1. That oil kept at the temperature of 70° C., for eight hours, has its drying property considerably increased.

"2. That, if peroxide of manganese be added to the oil kept at this temperature, it becomes sufficiently drying for use.

"3. That a very drying oil will be obtained by heating linseed oil, for three hours only, with 15 per cent. of metallic oxide, and at the temperature generally adopted by color merchants.

"My experiments explain perfectly well the rôle of linseed oil, or more generally speaking, of drying oils, in painting. Indeed, when oleic acid is mixed with metallic oxides which may solidify it, it passes instantaneously from the liquid to the solid state, and there is no uniformity in the ensemble of the molecules of the oleate. The effect is different when a drying oil, absorbing oxygen, passes progressively to the solid state. The slowness with which the change takes place allows of the symmetrical arrangement of the oily molecules, which would appear transparent if there were not opaque molecules between them. But if the latter do not predominate, the arrangement is such that the painting is glittering, and even brilliant, because the light is reflected by the dry oil as by a looking-glass.

CHAPTER IV.

BRONZING.

Certain articles of plaster of Paris, wood, paper, and pasteboard, are given a bronze color, which varies with the kind of bronzing stuff employed, and which more or less resembles real bronze.

1. A very brilliant bronzing is done with the cuttings of gold-beater's foil, ground under a muller with honey. The object to be bronzed is coated with linseed oil, and the metallic powder is applied upon it with a rag.

2. Mosaic gold (*aurum mussivum*) may be employed for the same purpose, after having been finely ground with 6 parts of calcined bones. A small quantity of this mixture is taken upon a wet cloth and applied upon the object. The bronze coat is then rubbed with a dry rag, and afterwards burnished.

When mosaic gold is to be applied upon paper it is not mixed with calcined bones, and the size is the white of egg or a thin alcohol varnish. The bronze is applied with a brush, and is afterwards burnished.

3. When a clean piece of iron is immersed in a hot solution of sulphate of copper, it soon becomes

covered with a precipitate of metallic copper, which, after being washed, is ground with six times its weight of calcined bones, and may be used for bronzing in the manner before explained.

4. Sometimes it is desired to cover articles with a gray color, resembling that of iron, and which is called *white bronze.* An agreeable appearance is imparted by *argentum mussivum;* but finely-powdered tin is also used. This powder is prepared by pouring molten tin into a box, the sides of which have been well rubbed with chalk, and shaking the metal very rapidly and continuously until it has become cold. This powder, passed through a silk sieve, and sized with a solution of glue, is applied with a brush. The coat has a dead lustre, which may be rendered bright by burnishing.

The *argentum mussivum* is prepared with equal parts of bismuth, tin, and mercury.

When plaster of Paris is to be bronzed a gray color, it is rubbed with plumbago.

5. When cleansed and scoured cast-iron is dipped into a weak solution of sulphate of copper, it becomes covered with a film of metallic copper, which is quite adhesive. In this case, the hue of the copper is reddish, passing to a brown yellow.

SECTION I.

REAL BRONZE, COLOR WHICH IT ACQUIRES IN THE AIR.

Bronze, exposed to the air for a greater or less length of time, becomes covered with a very thin coat of carbonate, which imparts to it a greenish tinge, called old bronze (*patine*). Various processes have been proposed to produce this appearance in a short time;

but however close the resemblance may be, a practised eye will discover a difference. The lovers of antique bronzes should not complain of this result, since they posess a means of distinguishing really old articles from their imitations.

A color resembling more or less that of old bronze, is given to bronze ornaments and medals, by covering their surfaces with various mixtures.

SECTION II.

VARIOUS BRONZE COMPOSITIONS FOR METALS.

A great many compositions and pickles have been proposed for producing a desired *patine.* Several of these compositions have constantly given good results; but the success depends a great deal upon the mode of operation, and different operators, using the same composition, will often produce patines of different hues. The following are several of these recipes:—

The metal, turned or filed, is cleansed with nitric acid, and then covered with the mixture, which is uniformly applied by means of a soft brush, a rag, or a pad.

The nature of the alloy itself has a great influence on the bronze color obtained. Since, therefore, the alloys of articles for ornaments vary considerably, the same bronze composition, applied in the same manner, will give different results.

1. Nitric acid, diluted with 2 or 3 parts of water, is spread upon the article. The color appears gray at first, but afterwards it passes to a greenish blue.

2. The object is wet several times with a liquor composed of 1 part of sal-ammoniac, 3 of carbonate

of potassa, and 6 of common salt dissolved in 12 parts of boiling water, to which are afterwards added 8 parts of nitrate of copper. The coat is unequal and raw at the beginning, but it soon becomes softer and more uniform.

3. A handsome blue-green bronze may be obtained with concentrated ammonia alone with which the article is many times rubbed.

4. The basis of a great many compositions is vinegar with sal-ammoniac. Many skilful workmen never use anything else but a solution of 60 grammes of sal ammoniac in 1 litre of vinegar.

5. Another pickle, which gives very good results, is a solution of 30 grammes of sal ammoniac, and 8 grammes of sorrel salt, in 10 litres of vinegar.

6. A skilful chaser of Paris uses a mixture of 15 grammes of sal ammoniac, 15 of common salt, 30 of carbonate of ammonia, and 1 litre of vinegar.

7. Another good composition is: 15 grammes of sal ammoniac, 15 grammes of common salt, 15 of aqua ammonia, and 1 litre of vinegar.

A brush, dipped into this mixture, is rubbed upon the cleansed article until it has acquired a fine bronze color. The piece should only be moistened, and any remaining dampness is removed with another brush.

If, after two or three days, the coat appears too pale, the operation is begun anew. The work may be done in the open air, which causes the color to appear sooner. The metal never requires to be heated.

Good effects are also obtained with the two following compositions:—

8. Sal ammoniac and common salt, each, 8 grammes; aqua ammonia, 16 grammes; vinegar, ½ litre.

9. Sorrel salt, 2 grammes; sal ammoniac, 8 grammes; vinegar, $\frac{1}{4}$ litre.

This mixture is applied with a slightly moist brush, the application being continued until the desired tint is obtained. These compositions give a better coloration when the operation is conducted in a clear and aerated place, instead of a dark room.

Medals are colored in a somewhat different manner, and the pickles also greatly vary.

10. A thick paste is made in vinegar, of an intimate mixture of 500 grammes verdigris, and 333 grammes of sal ammoniac. A volume of this paste, about equal to a walnut, is boiled and stirred in a certain quantity of vinegar diluted with water. After a boil of fifteen minutes the liquor is allowed to settle, and is then decanted. The medals are boiled for five or six minutes in the clear liquor, and are afterwards well washed.

The same liquor cannot be used more than five or six times, and a small quantity of vinegar is added at each operation.

The boiling is effected in copper vessels, and the medals are separated from the vessel and from each other by means of small pieces of wood. The medals should be immediately wiped off after the coloring and washing, otherwise their hue will change. When they are perfectly dry, a bright lustre may be given to them by another stroke of the press.

It often happens that a portion of the medal acquires a bad color or is spotted.

11. The operation is conducted in the same manner with a mixture of 510 parts of verdigris, and 250 parts of sal ammoniac, ground on a slab with vinegar. The mixture is kept in well-closed vessels. When

it is needed for use, a small proportion of it, as in the previous recipe, is boiled for ten or twelve minutes in a tumblerful of vinegar diluted with 2 litres of water.

The alloys holding lead and tin are handsomely bronzed with a mixture of 100 parts of a neutral and pure solution of nitrate of copper marking 18° Bé., and 20 parts of sal ammoniac. The articles should be barely moistened with this liquor.

As a matter of curiosity, we here give the Chinese process for bronzing:—

The copper is washed with vinegar and wood ashes, until it is perfectly bright. It is then dried in the sun and smeared with the following composition: 2 parts of verdigris, 2 of cinnabar, 5 of sal ammoniac, 2 of the beak and the liver of a duck, and 5 of alum, the whole thoroughly mixed and made into a thin paste with water. The smeared copper article is then heated, cooled, and wiped off. The operation is repeated eight or ten times. The copper acquires a handsome appearance, and the bronzing is so durable that it loses nothing of its beauty by exposure to the rain and air.

A fine bronze may be obtained with a mixture of 1 part of sal ammoniac, 3 parts of cream of tartar, and 3 of common salt, the whole being dissolved in 12 parts of hot water, to which are added 8 parts of a copper solution.

By increasing the proportion of common salt, the coloration is lighter and tending towards yellow; by diminishing or suppressing it entirely, the coloration is bluish. The action is more rapid if the mixture contains more sal ammoniac.

There are certain articles for which a red bronze is desirable, and which are smeared with oxide of iron. If these pieces be rubbed nearly dry with a liquor holding about $\frac{1}{30}$ of sulphide of potassium, and then exposed to the fire, the coloration turns to a greenish-brown.

SECTION III.

RECIPE FOR THE ORDINARY BRONZE OF THE FOUNDERS.

Take—

Strong vinegar	1 litre.
Sal ammoniac	30 grammes.
Alum	15 "
Arsenious acid (white arsenic)	8 "

Mix the whole together, and when the salts are dissolved, the liquor is ready for use. A good bronze is obtained from sal ammoniac alone, in vinegar, and many founders employ nothing else. Indeed, with a good alloy, success is almost certain.

After the casting, the metal is polished with a fine cut file, or upon the lathe, or with sand paper, or by a dipping in nitric acid. It is absolutely necessary, for the success of the operation, that the metal should be perfectly clean, and especially free from grease. Aqua fortis (nitric acid) is the best cleansing agent, and it should be employed when a handsome finish is desired. The other methods, however, are sufficient for ordinary work.

SECTION IV.

MODE OF APPLYING THE BRONZING MIXTURES.

The bronze mixture is applied with a small brush, and the articles should be kept constantly moist during the operation, in order not to become green.

When the desired color is obtained, which generally requires from 25 to 30 minutes, the work is rapidly passed through clear cold water, dried in tepid sawdust, and then varnished, in order to preserve the coloration.

It happens quite often that, on account of the quality of the alloy, the bronze composition does not produce a sufficiently dark coloration. The following is the best manner of remedying this inconvenience:—

Take about 8 grammes of the best lampblack, stir it with about one tumblerful of rectified alcohol, and pass the liquor through a cloth. The piece upon which the bronze composition has been applied, should be heated upon a metallic plate or before a clear fire, until it can scarcely be held in the hand. Then, with a camel's-hair brush, thin coats of the lampblack liquor are spread upon it, so long as the desired tone is not yet reached.

When the coats have become entirely cold, they are polished with a very soft brush, or with a rag dipped in very limpid green oil. The whole is then varnished, and thus is obtained the finest bronze color which can be imparted to an alloy of zinc and copper. If the mixture of lampblack be not too black, and the varnish of too light a yellow, the color of the bronzed alloy will be of a splendid deep green. We may infer from it, that it is possible to obtain all the tones of *green bronzes* by using more or less of the lampblack mixture, employing a varnish more or less yellow, and giving a greater or less thickness to the coats of black. However, the article will keep its color longer, if the coat due to the bronze composition be made dark enough to dispense with the lampblack. This can be done, but more time is required than when the black is employed.

SECTION V.

MODE OF GIVING THE PROPER BRONZE COLORATION WITHOUT LAMPBLACK.

When the coat of bronze color is dry, if the tone does not appear deep enough, the piece is placed before a bright fire, or exposed to the rays of the sun, and its position is now and then changed; while at the same time, a draft is avoided. The piece is then rubbed with a soft brush, and a very handsome bronze is thus obtained. This method is somewhat tedious, and, in case of hurry, lampblack is more advantageous.

SECTION VI.

BRONZING OF GUN BARRELS.

They are rubbed rapidly with melted butter of antimony, and the operation is repeated several times. The barrels should be moderately heated.

SECTION VII.

BRONZING PLASTER OF PARIS.

Articles of plaster of Paris may be mistaken for old bronze (provided they are not handled), if they be impregnated with a copper soap proposed by MM. d'Arcet and Thénard. The following is the mode of operation:—

Pure linseed oil is converted into a neutral soap, by means of caustic soda. A concentrated solution of common salt is then added, and the boiling is continued until the liquor becomes very dense, in order that the grains of soap shall come to the surface. The soap granules are collected upon a cloth, drained and pressed, so as to deprive them, as far as practicable, of the adhering lye. The soap is then dissolved in pure water, and the solution filtered through a cloth. Another solution is made, also in pure water, of 80 parts of sulphate of copper, and 20 parts of sulphate of iron, which is filtered, and which receives the soap water until the decomposition is complete. A small quantity of a solution of the two sulphates is then added, the whole is well stirred and boiled, and, in this manner, the metallic soap is mixed with an excess of the sulphates. The precipitate is thoroughly washed with boiling water, and then with cold water. It is collected upon a cloth, drained, and dried as completely as possible.

On the other hand, 1 kilogramme of pure linseed oil is boiled with 250 grammes of finely powdered litharge, then filtered through a cloth, and allowed to settle in a hot room.

A mixture is then made in a stoneware pot, placed upon a steam or water-bath, of 300 grammes of boiled linseed oil, 160 grammes of the metallic soap, and 100 grammes of pure white wax. The whole is kept heated long enough to remove all dampness. The article of plaster of Paris is also heated at from 80° to 90° C., in a stove, and is covered with the hot mixture. When the plaster has become too cold for the mixture to penetrate, it is again heated to the same temperature, and consecutive coats of the composition are thus applied until the plaster of Paris no longer absorbs it. The piece is again heated in the stove for a few minutes, in order to absorb the composition which may remain on its surface. The natural porosity of plaster of Paris is such, that the mixture will be absorbed without impairing the sharpness of the finest parts of the cast. The mixture will penetrate more or less deep, according as the operation is more or less often repeated.

When the piece has acquired the desired color, a lustre is given by rubbing it with a pad of cotton. In order more exactly to imitate the real old bronze, the raised parts are touched with shell gold (ground gold foil). This process allows of a thorough imitation of medals, statuettes, vases, etc. The plaster, which has been thus prepared, resists dampness perfectly well, and becomes very durable.

SECTION VIII.

GREEN BRONZE.

Take—

Strong vinegar	1 litre.
Mineral green	15 grammes.
Umber	15 "
Sal ammoniac	15 "
Gum Arabic	15 "
Avignon berries	60 "
Green copperas	15 "

And about 85 grammes of green oats, if they can be had, but they are not absolutely necessary. Dissolve the salts and the gum in separate portions of the vinegar, then mix the whole in a stoneware pot. Add the Avignon berries and the oats, and boil upon a gentle fire. After cooling, filter through a flannel bag. The liquor is then ready for use.

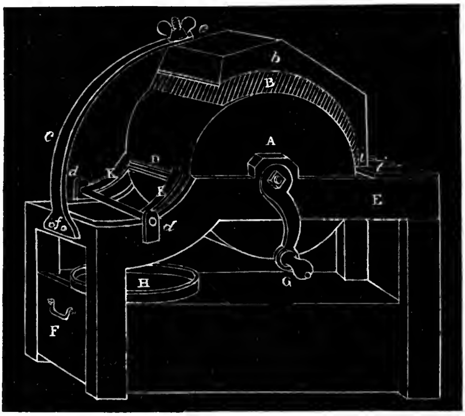
APPENDIX.

Mill for grinding colors.

This machine, invented by Mr. Rawlinson, is very simple. It is intended especially for neutralizing the dangerous effects of the dust of lead pigments, which is produced in great quantity in the ordinary process of grinding upon a slab.

This mill is represented in Fig. 62.

Fig. 62.



A is a solid cylinder, 45 centimetres in diameter, and from 12 to 15 in height. It is generally made of black marble, which is harder and more easily polished than other stones.

B is a concave muller, of the same material as the cylinder, which it covers for about one-third of the circumference. It is absolutely necessary that the curvature of this muller corresponds exactly with that of the cylinder. It is covered with a wooden cap *b*, held by hinges *i i*, to the frame E.

The area of this muller, in contact with the cylinder, is about 6 times that of an ordinary muller; therefore the useful effect and the economy of labor in its use are as many times greater.

Moreover, the motion of the machine is more rapid than that of the ordinary hand muller, and there is less fatigue for the operator.

We should observe that the machine here described is of the smallest pattern, and that a man of ordinary strength may easily move a cylinder from 60 to 65 centimetres in diameter, and have his production increased in the same proportion.

C is a bent piece of iron, firmly fixed at *f*. It acts as a pressure spring upon the muller, and the pressure is regulated by a screw *c*.

D is a scraper, movable around the points *d d*, and inclined upon the cylinder. However, it is put in this position only when it is desired to clean the stone, which is then revolved in a direction opposite to that followed during the grinding proper. This scraper is arranged like a saw upon four pieces of wood K K; its blade is formed of a steel spring for clocks.

E. Wooden frame, supporting the apparatus and the hand crank.

F. Drawer for the cleaning knives, those knives used by curriers being the best.

G. Sliding board upon which the color falls.

H. Metallic dish for receiving the scrapings.

No pigment is put upon this mill, unless it has previously been powdered in a cloth-covered mortar, or in a mill for dry grinding. This first preparation is not new, and is as necessary as in the old mode of grinding.

When the color has been mixed with water or oil, it is carried by a spatula upon the cylinder near the muller. More play may be given by loosening the screw *c;* but this is not necessary, because paint may be added by successive quantities, until, after several revolutions, the cylinder is entirely covered.

When it is desired to clean the muller, the screw *c* is loosened, and the wooden cap is thrown backwards around the hinges *i i*. The muller-stone may then be removed.

A few revolutions of the cylinder, with the cleaning knives pressed against it, are sufficient to clean it thoroughly.

It is impossible to state in advance the quantity of color which should be put upon this mill, or how long it should stay there, since the only rule is the desired degree of comminution. But experience has proven that as much work is done with this apparatus in three hours, as in a whole day with the ordinary flat slab and muller, and that the waste is much less.

The author adds:—

1. That a fly-wheel, fixed at the other end of the crank axle, will render the motion more uniform.

2. When the pigment is very hard, it is advisable to increase the pressure of the muller, and to diminish the velocity of the rotation of the cylinder.

3. Too great a velocity is prejudicial to the brightness of delicate colors, especially when the stones become hot.

The inventor also recommends a process for preparing the bladders for oil colors. A small wooden peg is inserted in the neck of the bladder, and a string is tied upon it. By removing the peg and pressing the bladder, the color runs out upon the pallet. It will be still better to tie the bladder upon a quill, with the point on top, because by cutting it, the color may be squeezed out. The drying of the color remaining in the bladder will be prevented by plugging the quill with a small wooden pin. This method is cleaner and more economical than that of perforating the bladders with a knife blade.

Mill for dry indigo.

Fig. 63 represents an ordinary mortar L, made of marble or of some other hard stone, in which revolves a muller M, which is pear-shaped.

Fig. 63.

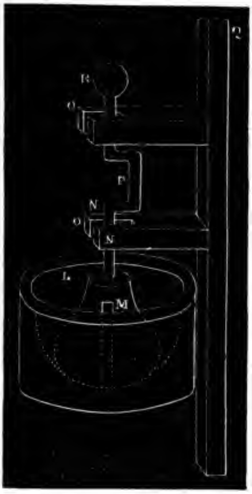


Fig. 64.

Its axis revolves at N N, upon two pieces of oak wood fastened to the wall Q. Pins are put in *o o*, in order to retain the axis in its place. P is the crank handle. R is a movable weight, which is added when it is desired to increase the weight of the muller.

Fig. 64 represents the muller and its axis removed from the mortar. The lower curve of the muller should correspond with that of the mortar. S is a deep groove in the muller.

A certain quantity of coarsely broken indigo is put into the mortar, and the rotary motion of the muller causes the pieces to fall into the groove, and to become finely ground. The operation will be rendered more easy, if the lower part of the groove be made slightly wider.

By covering the mortar with two pieces of wood meeting in the middle, and having a hole for the passage of the axis, no dust will escape.

In manufactories the mill is turned by steam power.

The weight R is sometimes replaced by a fly-wheel, which renders the motion more uniform, and which should not be more than 60 to 65 centimetres in diameter, if made of cast-iron. If this fly-wheel acts at the same time as a driving pulley, the strap should be about 10 centimetres wide.

Improvements in the manufacture of oils, varnishes, and colors, by MM. H. Bessemer and J. S. C. Heywood.

The improvements which we are going to describe are principally:—

1. A mechanical apparatus for extracting oils and oleaginous substances from the materials in which they are held.

2. A peculiar treatment of these oils and oleaginous substances, still combined with the materials

which produce them, by pure water or alkaline solution, and by hydraulic pressure in closed vessels.

3. A mode of regulating the heat applied to varnish vessels; by means of a metallic or air-bath; a method of exhausting and condensing the vapors of resins and oils used in the manufacture of varnishes; and lastly, a mode of boiling oils for the preparation of colors.

4. A process for giving more body and opacity to colors produced by the combination of silica with an alkali, alkaline earths, or metallic oxides, and making vitrified colors from them.

5. An apparatus or mill for grinding these colors.

I. In regard to the mechanical apparatus for extracting oils and oleaginous substances from the materials in which they are held; we use the oil press represented by the following figures:—

Fig. 65 is a side view of the apparatus.

Fig. 66 is a horizontal projection of the apparatus.

Fig. 65.

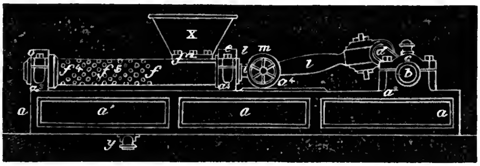


Fig. 66.

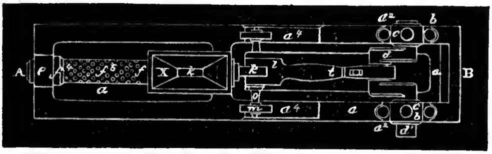


Fig. 67 is a longitudinal section passing through the axis.

Fig. 68 is, on a larger scale, a horizontal section of part of the cylinder.

Fig. 67.

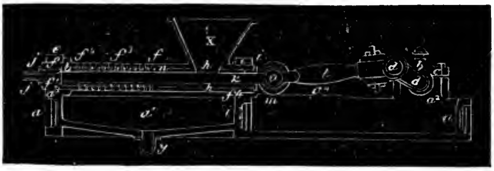
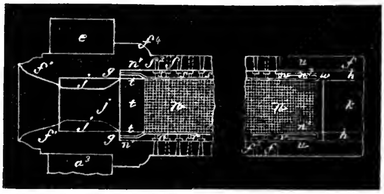


Fig. 68.



The frame a a, of one solid casting, is basin shaped at a^1a^1, in order to receive the oily substances which run into it during the pressing; a^2a^2 are the pedestals and journals, in which the crank axle d revolves. On the opposite side the pedestals a^3a^3 and their caps e e, maintain the pressure cylinder $f f^1$, which is made of ordnance bronze, thick enough to resist a considerable internal pressure. This cylinder $f f$ is doubled inside with a bronze pipe n, the outside of which is spirally grooved like a screw, the square threads of which are very close. Small conical holes f^3 f^3 are bored in the groove, and through the whole thickness of the pipe n. At n^1n^1, the internal diameter of the pipe is greater, and is filled with the steel ring t t. The other diameter n^2n^2 is smaller, and is provided with an external steel ring u u. A cylindrical sack v v, open at both ends, and made of fustian, hair cloth, or of any analogous permeable substance, fits the inside of the pipe n, and contains another cylinder w, of wire-cloth or of finely perforated sheet iron. All these inside fittings are stretched and maintained firmly by the steel rings t u. The cylinder n is then introduced into $f f^1$, as far as the recess g g, and the tubular piece h h is brought in contact with the ring u. The screwed plug i, acting also as a stuffing box, maintains the whole tight.

The extremity $f^1 f^1$ of the cylinder is of a smaller diameter, and contains the ring j j, the diameter of which regulates the pressure supported by the materials operated upon. A solid piston k fits the inside of n, and receives its to and fro motion from the connecting rod l. The parallel motion is kept up by the small wheels m m, rolling upon the guides a^4 a^4, of the bed frame. X is a hopper, bolted upon the collar f^2 of the pressure cylinder, and which delivers its contents when the piston k has left the opening free. $f^3 f^3$ are holes perforated in the pressure cylinder, and communicating with those of the doubling pipe n. The oil escapes through them. $f^4 f^4$ are rings maintaining the cylinder firmly pressed against the pedestals a^3 a^3.

When steam power is directly employed for giving motion to the piston of the press, the connecting crank placed at d^1 should be fixed at such an angle that, when the piston k is at the end of its course, the piston of the steam engine is only half way up, that is, when the power of the steam admitted is the greatest. In this manner, when the steam engine passes by its dead points, the piston k is half way in its return motion. When another motive power is applied for turning the crank d it becomes necessary to put a fly-wheel upon the axle d^1.

When this apparatus is employed for the extraction of linseed oil, the seeds are ground and heated in the ordinary manner, and then introduced into the hopper. Each time that the piston *k* goes back, the opening under the hopper is left free, and a certain quantity of seeds fall into the tube *n*. When the piston returns, it pushes these seeds towards the narrow part of the cylinder, and, as the friction resulting from the narrow passage through the ring *j* is great, the pressure upon the seeds is also considerable.

This ring *j* is movable, and may be replaced by others having a greater or less diameter, as it is desired. The doubling pipe *n* may also be entirely removed for the necessary repair of worn-out parts.

The action of the piston *k* resembles that of the piston of a hydraulic press; the seeds are pumped in on one side, and pressed out on the other. All that portion of the cylinder where the seeds are held is lined with hair-cloth or any other permeable and resisting substance. Rents and other damages are not frequent, since the cloth is protected on the outside by the tube *n*, and on the inside by a metallic cloth, or a piece of perforated sheet-iron.

The pressed oil passes through the above linings, then through the holes of the inside tube and of the cylinder, and lastly falls into the basin *a′*. It may be removed by the pipe *y*.

Although this description is that of a single pressure cylinder, it is evident that several of them may be fixed upon a common frame, and their pistons be set in motion by the same power. In this case, the cranks will be set at such an angle that the resistance will be nearly uniform. We prefer a cylindrical form for the piston and the cylinder; but any polygonal shape will do just as well.

In the foregoing description of the oil-press, we have not indicated any mode of heating the oily substances; but, as it is sometimes necessary to raise their temperature, we will give the manner of doing it.

A greater length and a greater diameter are given to the pressure cylinder, and the basin *a'* is divided into two distinct compartments. A strong wrought-iron pipe is introduced into the axis of the cylinder through the open end, and reaches about midway towards the hopper. The extremity of the pipe inside of the cylinder terminates in a point, while the other rests against a framework, which gives it the power of resisting the pressure tending to push it out of the apparatus. No steam escapes into the cylinder, since the pipe is not perforated.

The ground seeds which fall from the hopper are pressed first in that portion of the apparatus where the pipe does not reach, and give out a certain proportion of cold oil, which is collected in the first compartment of *a'*. Being pressed further on, the seeds are obliged to pass through the annular space between the steam-heated pipe and the cylinder. There the oily paste absorbs the heat rapidly, and abandons a proportion of oil, which falls into the second compartment of *a'*. We see, therefore, that the two operations of cold and hot pressing are effected simultaneously.

II. Our mode of extraction of oils and oleaginous substances still contained in the vegetable or animal materials, by a treatment with pure water or alkaline solutions, and with hydraulic pressure in closed vessels, has been applied with the apparatus which we shall now describe.

Fig. 69 is a longitudinal view, and Fig. 70 a longitudinal section of the apparatus.

Fig. 69.

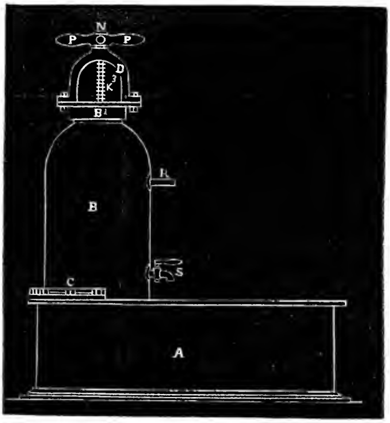
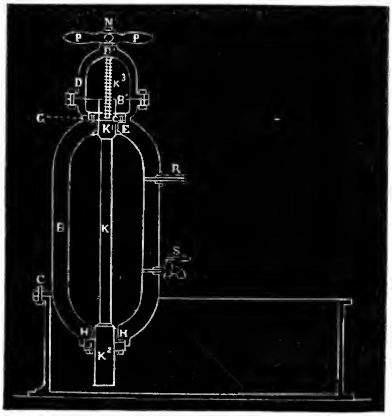


Fig. 70.



A is a cast-iron reservoir, rounded at the ends, and open on top. B is a cylinder with hemispherical ends, fastened to A, and able to resist a pressure of 36 atmospheres. This cylinder is kept in a vertical position by a collar C, which forms a half circle, and is fastened by bolts upon a similar collar cast on A. The upper part of the vessel B forms a cup B^1, the flange of which supports a bracing iron hook D. The neck, connecting the cup and the vessel B, is lined with a doubled-up leather E, maintained by the ring G. The bottom of the vessel is also provided with another doubled-up leather H, maintained by the bolted ring J. A stout iron rod K extends from the bottom of B up to the top of the bracing hook D. The portions K^1 K^2 are of a larger diameter and fit the doubled-up leathers. The upper part of K has a square thread K^3, cut upon it, which passes through D^1, and is seized by the nut N, moved by the handles P P. In this manner the rod K may be raised or lowered.

R is a tube, through which water may be injected into the vessel B, by means of a pressure pump, similar to those employed for hydraulic presses. S is a stopcock used for letting out a part of the contents of the vessel, or removing the pressure when it is necessary to do so. The areas of the stoppers K^1 and K^2 being equal, the pressure exerted inside of the vessel has no tendency to push the rod either up or down, and the doubled-up leathers make a tight joint.

After a certain portion of oil or oleaginous substances has been extracted from the vegetable or animal materials, the remaining portions are more difficult to obtain, and are treated in the following manner. The materials are removed from the press, and then mixed with a certain proportion of hot water, or of a slightly alkaline lye, in order to make a semi-fluid paste, which is introduced into the above described apparatus. By turning the handles P P, the stopper

K^1 is raised above the opening of the cup, whereas the lower one K^2, which is much longer, keeps the bottom aperture closed. The semi-fluid materials are then introduced into the cup B^1, which delivers them into the vessel B. The rod K is lowered, so as to close the two apertures, and the hydraulic pump being set in motion, the materials are soon submitted to the required pressure.

The whole is allowed to stand for a few minutes, in order to effect the reaction; then the stopcock S is opened, and a portion of the substances fall into the reservoir below. By moving the handles P P, the stopper K^2 is raised high enough for the remainder of the substances to flow out. The rod K is lowered again, and a new charge is put into B.

The pressure exerted upon the mixture of oleaginous substances and water forces the inclosed oil to make with water a liquor of a milky appearance, from which the oil may be separated, either by settling in large tanks, or by evaporating the water.

When the oils are intended for the manufacture of soap, or for certain other uses, the mixture needs not to be separated. When seed oil is thus obtained, the mucilaginous substances favor the combination of the two liquids.

As soon as the materials have been removed from the reservoir A, they are drained upon sieves, and the solid portions are again pressed for extracting the fluid portions. In certain cases, it is advantageous to boil the milky liquor, in order to coagulate the albuminous substances, and facilitate the purification of the oil.

III. The following is the process which we use for regulating the heat applied to varnish vessels by means of metallic or hot air baths; and our method for exhausting and condensing the vapors disengaged from resins and oils, during the manufacture of varnishes, or from boiling oils employed for the preparation of colors.

In the actual method of preparing varnishes, the resins and gums are generally liquefied in thin copper pots, placed directly over the fire. The temperature may be suddenly raised so high that the gums are seriously damaged, and often catch fire. On the other hand, equally rapid coolings may produce other inconveniences. Moreover, at the high temperature required for melting copal, amber, resin anime, and other analogous substances, their more volatile portions form abundant fumes. The disengagement of these vapors affects the men powerfully, and sometimes is the cause of dangerous explosions. On the other hand, the value of these lost vapors is considerable, either for the manufacture of varnish or for other uses. The melting pots must remain open, in order to watch the operations, and to add fresh portions of the materials. These considerations show how difficult it has been to prevent the losses by volatilization, and have caused us to search for the process which we are about to explain.

Figs. 71 and 72 are vertical and horizontal sections of the apparatus for melting the resins or gum resins.

a is the fireplace, placed below the floor of the work-room as usual; *b* is the door of the fireplace, and *c*, the ash pit. Upon this fireplace there is placed a cast-iron kettle *d*, nearly filled with an alloy of equal parts of lead and tin, because the melting point of lead alone is too high for our purpose. The flame passes through the flues *e* and *f* around the kettle:

g is the melting pot, made of thin copper, and riveted to the collar *h*. The pot is held in the bath by three iron hooks *i*, *i*, *i*, which pass into corresponding places cut in the collar *h*; and the fastening is effected by partly turning the pot.

Fig. 71.

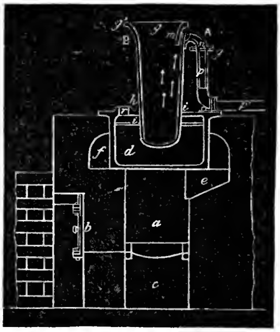
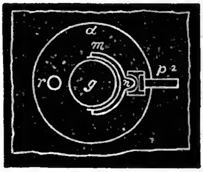


Fig. 72.



On top of the pot there is a kind of hanging lip *m*, occupying one-half of the circumference, and standing at about the distance of 12 millimetres from the inward surface of the pot. The opening thus left on the side of the pot is covered with a riveted semicircular conduit, which at *n* connects with the pipe *p* p^1. The pipe p^1 is attached to a cooling worm, placed in a tub of cold water, and the outlet from the worm terminates in a vertical pipe, the lower part of which is closed with a stopcock and receives the condensed products, while the upper part is connected with an exhausting apparatus, which is constantly aspiring the vapors into the cooling worm, and delivers into the air the uncondensable products. The following is the manner of using the apparatus.

When the fire is lighted, and the metallic bath is in fusion, a thermometer is introduced through the opening *r*, and the temperature noted. As soon as the required temperature is reached, the melting pot *g* is put into the bath, and fastened by the hooks *i*, care being taken that the tubes *n* and *p* should correspond. A charge of 14 kilogrammes of amber, for instance, is then introduced into the pot, watched, and stirred in the ordinary manner. The exhaust is also set in motion, and the *amber oil*, or volatile portion of the amber, follows the direction of the arrows, being drawn by suction under the lip *m*, and from thence into the cooling worm, accompanied by a certain proportion of air.

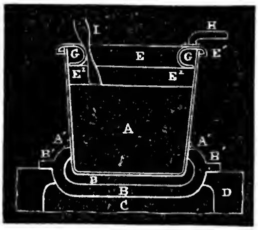
There is no great difficulty in maintaining a suitable and uniform temperature in the metallic bath, because, in the short time necessary for melting a charge, the temperature of a considerable quantity of metal does not change sensibly, even should the fire be much urged, or allowed to die out. Besides, an excess of heat may be reduced immediately, by introducing a large piece of cold iron through the opening *r*, and leaving it in the bath for one or two minutes. In general, we may feel confident that the temperature will remain constant during one operation, unless the fire be entirely neglected.

When the resin is melted and mixed with oil, it should be removed from the metallic bath into the boiling pot. The contents are poured from the side g^1.

Thus, in this manner of melting resins, the heat has been easily regulated without escaping fumes, and with a condensation of volatile products, which may be utilized advantageously by the varnish maker.

Fig. 73 is a vertical section of the pot for boiling oils, gums, and resins in the manufacture of varnishes. The same pot may also be employed for boiling the oils employed in the preparation of paints.

Fig. 73.



A, copper pot of the ordinary shape; B, flat cast-iron pan, which is made very thick, in order to stand and retain the heat, and thus to counterbalance rapid changes in the temperature of the fire. This pan is kept over the fireplace C, by means of the flange B′ B′, which rests upon the brickwork D. The copper pot is held upon the air bath, by means of the riveted flanged ring A′. The cover of the pot is an annular inverted gutter E, the curvature E^2 of which has its edge quite close to the sides of the pot, without, however, touching them, and is connected by means of the tube H with a cooling worm and an exhaust. The mode of operation is as follows:—

The heat of the fireplace C is transmitted to the pan B, and the air contained therein communicates its temperature to the boiling pot, which, therefore, is not so much exposed to irregularities of temperature as if it were, as usual, placed directly over the fire. The suction exerted in the pipe H and the annular space G, carries away the vapors emitted by the boiling oils or varnishes, and forces them to pass through the cooling worm, where the condensable portions are collected. At the same time, the large aperture left in the annular cover permits of the watching of the operation, and of the stirring of the substances with the spatula I.

As this shape of the air bath requires the lifting upwards of the pot before it is removed from the fire, it may be more handy to give to this air-bath the shape indicated by the Figs. 74 and 75. J is a thick piece of cast iron with a ring and six radial ribs K K projecting above. The spaces Q form the air-bath, L is the fireplace; M, the brickwork of the furnace, and N, the bottom of the copper pan, which is level with the top of the furnace. In this manner the pot may be made to slide horizontally from the hot cast-iron without lifting it.

Fig. 74.

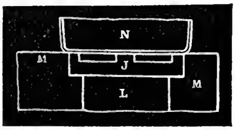
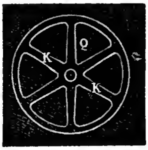


Fig. 75.



It is evident that a metallic bath could be employed for heating the oil pot, or an air-bath for dissolving the resins, but we believe that the described dispositions are sufficient.

IV. Our processes for giving more body or opacity to the colors produced by the combination of silica with alkalies, alkaline earths, and metallic oxides, and therefore making vitrified pigments, will be easily understood by the following description:—

In several arts, in painting on porcelain and glass, for instance, the colors employed are formed of the materials we have indicated. In certain cases, it is not absolutely necessary that the colors should be opaque, and in glass painting, on the contrary, transparency in the colors is a desideratum. The colors formed by the combination of silica with alkalies, alkaline earths, and metallic oxides, are remarkable for their resistance to the action of air and dampness; therefore, it is desirable that they should be employed in ordinary painting, but it is also absolutely necessary that they should possess sufficient body and opacity to cover well the materials upon which they are applied.

It is known that several kinds of glass, especially those which contain a great proportion of lime, will have their molecular arrangement completely changed by a long exposure to a not very intense red heat. From an ordinary transparent glass, they will become a semiopaque material, known under the names of *devitrified glass* or *Réaumur's porcelain*. Basing ourselves upon this fact, we propose the following mode of operation:—

We introduce into an ordinary glass pot a mixture of 250 kilogrammes of white sand, 100 kilogrammes of dry sulphate of soda, 85 kilogrammes of phosphate of lime, and 4 kilogrammes of charcoal, the latter being added for decomposing and removing the acid of the sulphate of soda. We pour the melted mixture, by means of an iron ladle, into cold water, and the suddenly cooled glass is reduced to small fragments, which are immediately heated for three or four days at from 370° to 480° C., in ordinary gas retorts. The hot fragments are then again raked into cold water. They become still more disintegrated, and are so brittle that they are easily powdered under ordinary vertical running stones.

The devitrification operated in the retorts, at a low and protracted heat, still increases the opacity due to the phosphate of lime. In certain cases, when an extreme degree of opacity is desired, a suitable proportion of oxide of tin is added.

The previously indicated mixture gives a white opaque glass which may be used as a basis for all the desired colors.

It is well known that metallic oxides are generally employed for coloring glass; these oxides are, therefore, combined with the above materials before their fusion in the glass pots, and in proportions to suit the desired hues or tones of color. We shall not here examine these proportions, since our present object is to give sufficient body and opacity to vitreous compounds, in order to use them with water or oils as ordinary paints.

In the proportions indicated for the formation of the vitreous basis, it is possible, if so desired, to effect certain changes; for instance, potassa may be substituted for the soda, as many glass manufacturers do. We have simply given the recipe which has appeared to us the most economical, and have indicated the sulphate of soda, which is very cheap in comparison with the carbonates of soda and potassa.

In order to bring the devitrified colors to the proper degree of comminution, they are first powdered under a vertical running stone, and then ground with oil or water in a color mill. This grinding should be done with the greatest care, and, in order to arrive at this result, we propose the apparatus or mill we are about to describe.

V. The ordinary mill for grinding colors is composed of a pair of horizontal stones, the lower one of which is stationary, while the upper one revolves on its axis. The color is furnished from a hopper, which delivers it into the central hole of the running stone;

and when this color has passed between the stones, it is received into a gutter, fixed to the bed stone. Each portion of the running stone traverses a space proportional to its distance from the centre; therefore at each revolution, the points near the centre travel less than those near the circumference. It follows that the stones must wear unequally, and that their action must become very imperfect, since the central portions, being but slightly worn out, prevent a sufficient contact of the stones near their edges. Moreover, the simple movement of rotation of the upper stone upon the lower one produces a series of concentric ridges and hollows which prevent the intimate contact and the action of the stones upon the particles of material to be ground. The wear of the stones is rapid, and at the same time the grinding is very imperfect. In order to remedy these defects we have built the following mill:—

Fig. 76.

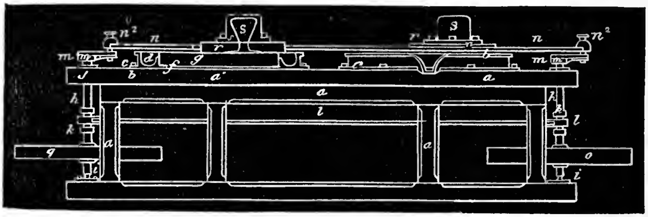
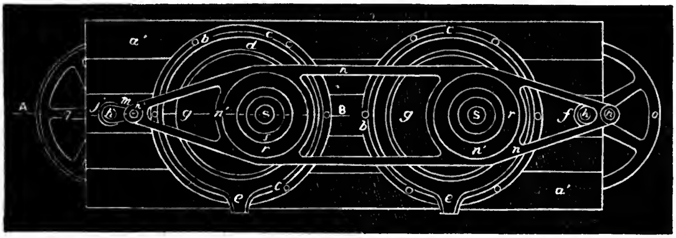


Fig. 76 is a side view of the principal pieces of the apparatus, and contains also a central section of one of the stones.

Fig. 77 is a horizontal view of the mill.

a a is a stout wooden frame, which, with the cover *a' a'* forms a kind of table, upon which are bolted two rings *b b*, with flanges *c c*. These rings are cast with a circular gutter *d*, for receiving the ground paint, which is drawn out by the lips *e e*. *f f* are the parts of the rings which support the bed stones *g g*, made fast with a cement of plaster of Paris. At each end of the frame *a a* there is a cranked axle *h*, revolving in the step *i*, and on top in the collar *j*. The cranks of the two axles are united by the connecting rod *l*. The upper extremities of the axles *h h* are fixed to ordinary cranks *m m*, the pins of which enter conical sockets n^2 n^2, of the movable frame *n n*, formed of iron bars inclosing two rings *n′ n′*. This frame acts also like a connecting rod. The cranks *k k*, connected by *l*, are at right angles with the cranks *m m*, so as to facilitate the passage of the dead points. The heavy pulley *o* receives the motion, transmits it to the whole apparatus by means of the connecting rod *l*, and of the rigid frame *n n*, and *q* acts as a fly-wheel.

Fig. 77.



The upper stones *r r*, resembling mullers, are provided with hoppers *s s*, and their lower surfaces are slightly bevelled near the centre to facilitate the introduction of the materials to be ground. These stones *r r* are placed in the rings *n′ n′*, where they have sufficient play, and press with all their weight upon the bed stones *g g*. When the semifluid materials are poured into the hoppers, and when the apparatus is set in motion, these stones *r r* are carried by the frame *n n*, and travel circles equal in diameter to that described by the cranks *m m*, besides their movement of rotation upon their own axis. It results from this compound motion, that all the points of their surfaces travel through equal spaces, and that the wear is equal in all their parts. In order to cause a constant change in the surfaces of contact, a play of 1 centimetre is left between the running stones and the enclosing rings *n′ n′*. This motion is the same as that used in certain mills for polishing plate glass. These stones, after being used for a certain length of time, become perfectly level, and therefore more effective, since no portion of the color can escape without having been ground between perfectly fitting surfaces. It is evident that the degree of comminution of the particles depends upon their more or less intimate and protracted contact with the grinding surfaces.

Description of an English mill for grinding colors.

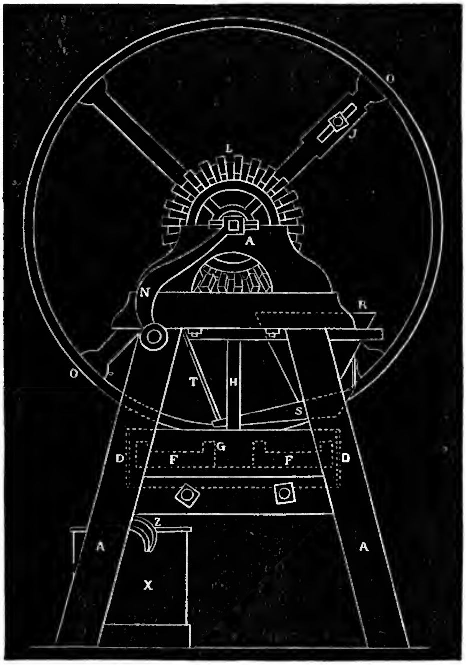
Fig. 78 is a view of the mill on the side of the crank handle; Fig. 79 is a front view of the same, and Fig. 80 a horizontal view from above.

The same letters designate the same parts in the three figures.

The frame A is of wood, strengthened by two iron bars B B. The bed stone C C is of cast iron, and its upper face has radial grooves like an ordinary millstone. It is fixed upon the iron bars B B, and is inclosed in a large iron ring D which prevents the color from running out except through the opening E. When the paint is sufficiently ground it is received in the vessel X placed underneath.

The running stone F is also of cast iron, and the dotted lines indicate its shape. The central hole G G and the circumference have a raised edge, high enough to prevent the color, inside and outside, from getting over them.

Fig. 78.



A vertical shaft H supports the running stone F and gives it its motion. The horizontal bevel wheel K is of cast iron, with twenty-seven wooden cogs, and is fixed to the top of the shaft H. Another vertical bevel wheel L, with twenty-seven cogs, is placed upon the horizontal axle M M and gears into K.

This horizontal axle M M carries at one of its extremities one crank handle N, and at the other end a fly-wheel O O which regulates the motion. One of

Fig. 79.

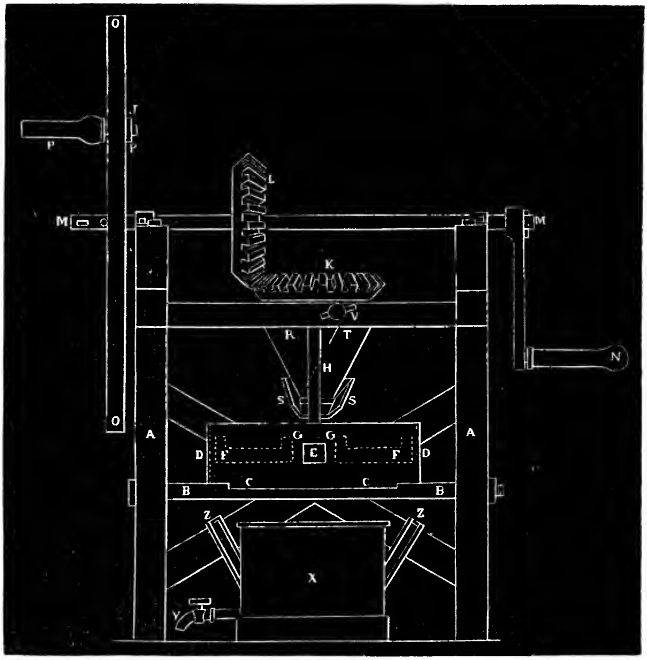
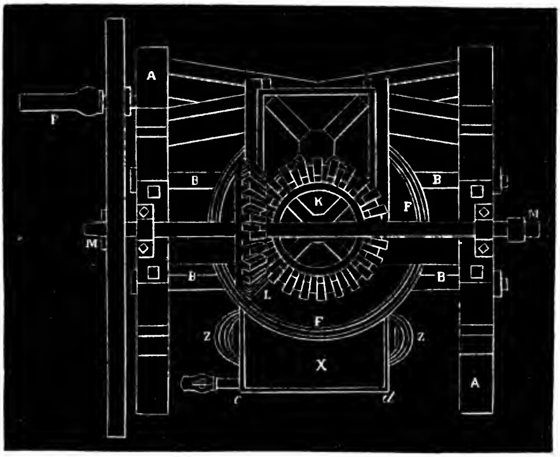


Fig. 80.



the arms of the fly-wheel also carries a handle P, which, if desired, may be used for turning the mill, and which may be fixed at the proper radius by the nut J.

The color to be ground is placed in the hopper R opening into the trough S, which delivers the material into the opening G of the running stone. A cord or chain T is wound up around the cylinder V, and presses the trough S against the square shaft H which shakes it continually. At the same time the proportion of material delivered is regulated by raising or lowering S by means of the cord T. The winding cylinder V is moved by the handle which traverses its extremity.

A copper box X receives the ground paint, and it is carried by the two handles Z Z. The paint may also be removed from this box by the stopcock Y.

Hermann's mill.

Mr. Hermann, of Paris, well known as a constructor of grinding apparatus, has invented a new machine for grinding paints in oil and in water.

Its disposition is remarkably simple, and consists of an eccentric stone of granite which is placed in a circular trough made of the same material or of other hard stone. The rotation imparted to that stone produces upon the materials held in the trough a circular and eccentric grinding, which constantly displaces the points of contact of the rubbing parts. In this manner colors and other products may be pulverized and ground with great perfection.

APPENDIX.

THE METRIC SYSTEM OF WEIGHTS AND MEASURES.

THE United States being the first to introduce the decimal system into the coinage of the country, and to demonstrate its superior utility, it is remarkable that we have hesitated so long in regard to the substitution of the same simple and rational system of weights and measures for the complicated and confused standards in general use.

In May, 1866, the Committee on Coinage, Weights, and Measures presented to the House of Representatives an exhaustive report, accompanied by bills authorizing the introduction of the *metric system* into the various departments of trade, and making all contracts, based on this system of weights and measures, valid before any court in the United States. They said:—

"THE METRIC SYSTEM.

"It is orderly, simple, and perfectly harmonious, having useful relations between all its parts. It is based on the METER, which is the principal and only arbitrary unit. The meter is a measure of length, and was intended to be, and is, very nearly one ten-millionth of the distance on the earth's surface from the equator to the pole. It is 39.37 inches, very nearly.

"The *are* is a surface equal to a square whose side is 10 meters. It is nearly four square rods.

"The *liter* is the unit for measuring capacity, and is equal to the contents of a cube whose edge is a tenth part of the meter. It is a little more than a wine quart.

"The *gramme* is the unit of weight, and is the weight of a cube of water, each edge of the cube being one one-hundredth of the meter. It is equal to 15.432 grains.

"The *stere* is the cubic meter.

"Each of these units is divided decimally, and larger units are formed by multiples of 10, 100, &c. The successive multiples are designated by the prefixes, *deka*, *hecto*, *kilo*, and *myria*; the subordinate parts by *deci*, *centi*, and *milli*, each having its own numerical significance.

"The nomenclature, simple as it is in theory, and designed from its origin to be universal, can only become familiar by use. Like all strange words, these will become familiar by custom, and obtain popular abbreviations. A system which has incorporated with itself so many different series of weights, and such a nomenclature as 'scruples,' 'pennyweights,' 'avoirdupois,' and with no invariable component word, can hardly protest against a nomenclature whose leading characteristic is a short component word with a prefix signifying number. We are all familiar with *thermometer*, *barometer*, *diameter*, *gasometer*, &c., with *telegram*, *monogram*, &c., words formed in the same manner.

"After considering every argument for a change of nomenclature, your committee have come to the conclusion that any attempt to conform it to that in present use would lead to confusion of weights and measures, would violate the early learned order and simplicity of metric denomination, and would seriously interfere with that universality of system so essential to international and commercial convenience.

"When it is remembered that of the value of our exports and imports, in the year ending June 30, 1860, in all $762,000,000, the amount of near $700,000,000 was with nations and their dependencies that have now authorized, or taken the preliminary steps to authorize, the metric system, even denominational uniformity for the use of accountants in such vast transactions assumes an important significance. In words of such universal employment, each word should represent the identical thing intended, and no other, and the law of association familiarizes it.

"Your committee unanimously recommend the passage of the bills and joint resolutions appended to this report. . . . . . The metric system is already used in some arts and trades in this country, and is especially adapted to the wants of others. Some of its measures are already manufactured at Bangor, in Maine, to meet an existing demand at home and abroad. The manufacturers of the well-known Fairbanks' scales state: 'For many years we have had a large export demand for our scales with French weights, and the demand and sale are constantly increasing.' Its minute and exact divisions specially adapt it to the use of chemists, apothecaries, the finer operations of the artisan and to all scientific objects. It has always been and is now used in the United States coast survey. Yet in some of the States, owing to the phraseology of their laws, it would be a direct violation of them to use it in the business transactions of the community. It is, therefore, very important to legalize its use, and to give to the people, or that portion of them desiring it, the opportunity for its legal employment, while the knowledge of its characteristics will be thus diffused among men."

TABLES

SHOWING THE

RELATIVE VALUES OF FRENCH AND ENGLISH WEIGHTS AND MEASURES, &c.

Measures of Length.

Millimetre = 0.03937 inch.
Centimetre = 0.393708 "
Decimetre = 3.937079 inches.
Metre = 39.37079 "
" = 3.2808992 feet.
" = 1.093633 yard.
Decametre = 32.808992 feet.
Hectometre = 328.08992 "
Kilometre = 3280.8992 "
" = 1093.633 yards.
Myriametre = 10936.33 "
" = 6.2138 miles.
Inch ($\frac{1}{36}$ yard) = 2.539954 centimetres.
Foot ($\frac{1}{3}$ yard) = 3.0479449 decimetres.
Yard = 0.91438348 metre.
Fathom (2 yards) = 1.82876696 "
Pole or perch (5½ yards) = 5.029109 metres.
Furlong (220 yards) = 201.16437 "
Mile (1760 yards) = 1609.3149 "
Nautical mile = 1852 "

Superficial Measures.

Square millimetre	=	$\frac{1}{645}$	square inch.
“ “	=	0.00155	“ “
“ centimetre	=	0.155006	“ “
“ decimetre	=	15.50059	“ inches.
“ “	=	0.107643	“ foot.
“ metre or centiare	=	1550.05989	“ inches.
“ “ “	=	10.764299	“ feet.
“ “ “	=	1.196033	“ yard
Are	=	1076.4299	“ feet.
“	=	119.6033	“ yards.
“	=	0.098845	rood.
Hectare	=	11960.3326	square yards.
“	=	2.471143	acres.
Square inch	=	645.109201	square millimetres.
“ “	=	6.451367	“ centimetres
“ foot	=	9.289968	“ decimetres.
“ yard	=	0.836097	“ metre.
“ rod or perch	=	25.291939	“ metres.
Rood (1210 sq. yards)	=	10.116775	ares.
Acre (4840 sq. yards)	=	0.404671	hectare.

Measures of Capacity.

Cubic millimetre	=	0.000061027	cubic inch.
“ centimetre or millilitre	=	0.061027	“ “
10 “ centimetres or centilitre	=	0.61027	“ “
100 “ “ “ decilitre	=	6.102705	“ inches.
1000 “ “ “ litre	=	61.0270515	“ “
“ “ “ “ “	=	1.760773	imp'l pint.
“ “ “ “ “	=	0.2200967	“ gal'n.
Decalitre	=	610.270515	cubic inches.
“	=	2.2009668	imp. gal'ns.
Hectolitre	=	3.531658	cubic feet.
“	=	22.009668	imp. gal'ns.
Cubic metre or stere or kilolitre	=	1.30802	cubic yard.
“ “ “	=	35.3165807	“ feet.
Myrialitre	=	353.165807	“ “

Cubic inch	=	16.386176	cubic centimetres.
“ foot	=	28.315312	“ decimetres.
“ yard	=	0.764513422	“ metre.

American Measures.

Winchester or U.S. gallon (231 cub.in.)	=	3.785209	litres.
“ “ bushel (2150.42 cub. in.)	=	35.23719	“
Chaldron (57.25 cubic feet)	=	1621.085	“

British Imperial Measures.

Gill	=	0.141983	litre.
Pint (⅛ gallon)	=	0.567932	“
Quart (¼ gallon)	=	1.135864	“
Imperial gallon (277.2738 cub. in.)	=	4.54345797	litres.
Peck (2 gallons)	=	9.0869159	“
Bushel (8 gallons)	=	36.347664	“
Sack (3 bushels)	=	1.09043	hectolitre.
Quarter (8 bushels)	=	2.907813	hectolitres.
Chaldron (12 sacks)	=	13.08516	“

Weights.

Milligramme	=	0.015438395	troy grain.
Centigramme	=	0.15438395	“ “
Decigramme	=	1.5438395	“ “
Gramme	=	15.438395	“ grains.
“	=	0.643	pennyweight.
“	=	0.0321633	oz. troy.
“	=	0.0352889	oz. avoirdupois.
Decagramme	=	154.38395	troy grains.
“	=	5.64	drachms avoirdupois.
Hectogramme	=	3.21633	oz. troy.
“	=	3.52889	oz. avoirdupois.
Kilogramme	=	2.6803	lbs. troy.
“	=	2.205486	lbs. avoirdupois.
Myriagramme	=	26.803	lbs. troy.
“	=	22.05486	lbs. avoirdupois.

Quintal metrique = 100 kilog. = 220.5486 lbs. avoirdupois.
Tonne = 1000 kilog. = 2205.486 “ “

Different authors give the following values for the gramme :—

Gramme = 15.44402 troy grains.
" = 15.44242 "
" = 15.4402 "
" = 15.433159 "
" = 15.43234874 "

AVOIRDUPOIS.

Long ton = 20 cwt. = 2240 lbs. = 1015.649 kilogrammes.
Short ton (2000 lbs.) = 906.8296 "
Hundred weight (112 lbs.) = 50.78245 "
Quarter (28 lbs.) = 12.6956144 "
Pound = 16 oz. = 7000 grs. = 453.4148 grammes.
Ounce = 16 dr'ms. = 437.5 grs. = 28.3375 "
Drachm = 27.344 grains = 1.77108 gramme.

TROY (PRECIOUS METALS).

Pound = 12 oz. = 5760 grs. = 373.096 grammes.
Ounce = 20 dwt. = 480 grs. = 31.0913 "
Pennyweight = 24 grs. = 1.55457 gramme.
Grain = 0.064773 "

APOTHECARIES' (PHARMACY).

Ounce = 8 drachms = 480 grs. = 31.0913 gramme.
Drachm = 3 scruples = 60 grs. = 3.8869 "
Scruple = 20 grs. = 1.29546 gramme.

CARAT WEIGHT FOR DIAMONDS.

1 carat = 4 carat grains = 64 carat parts.
" = 3.2 troy grains.
" = 3.273 " "
" = 0.207264 gramme
" = 0.212 "
" = 0.205 "
Great diversity in value.

Proposed Symbols for Abbreviations.

M—myria	— 10000	Mm	Mg	Ml	
K—kilo	— 1000	Km	Kg	Kl	
H—hecto	— 100	Hm	Hg	Hl	Ha
D—deca	— 10	Dm	Dg	Dl	Da
Unit	— 1	metre—m	gramme—g	litre—l	are—a
d—deci	— 0.1	dm	dg	dl	da
c—centi	— 0.01	cm	cg	cl	ca
m—milli	— 0.001	mm	mg	ml	

Km = Kilometre. Hl = Hectolitre. cg = centigramme. c. cm = $\overline{\text{cm}}^3$ = cubic centimetre. $\overline{\text{dm}}^2$ = sq. dm = square decimetre. Kgm = Kilogrammetre. Kg° = Kilogramme degree.

Celsius or Centigrade.	Fahrenheit.	Réaumur.
— 15°	+ 5°	— 12°
— 10	+ 14	— 8
— 5	+ 23	— 4
0 melting	+ 32	ice 0
+ 5	+ 41	+ 4
+ 10	+ 50	+ 8
+ 15	+ 59	+ 12
+ 20	+ 68	+ 16
+ 25	+ 77	+ 20
+ 30	+ 86	+ 24
+ 35	+ 95	+ 28
+ 40	+104	+ 32
+ 45	+113	+ 36
+ 50	+122	+ 40
+ 55	+131	+ 44
+ 60	+140	+ 48
+ 65	+149	+ 52
+ 70	+158	+ 56
+ 75	+167	+ 60
+ 80	+176	+ 64
+ 85	+185	+ 68
+ 90	+194	+ 72
+ 95	+203	+ 76
+100 boiling	+212	water + 80
+200	+392	+160
+300	+572	+240
+400	+752	+320
+500	+932	+400

1° C. $= 1^\circ.8$ Ft. $= \frac{9}{5}^\circ$ Ft. $= 0^\circ.3$ R. $= \frac{4}{5}^\circ$ R.

1° C. $\times \frac{9}{5} = 1^\circ$. Ft. 1° Ft. $\times \frac{5}{9} = 1^\circ$ C. 1° R. $\times \frac{9}{4} = 1^\circ$ Ft.

1° C. $\times \frac{4}{5} = 1^\circ$ R. 1° Ft. $\times \frac{4}{9} = 1^\circ$ R. 1° R. $\times \frac{5}{4} = 1^\circ$ C.

Calorie (French) = unit of heat } English.
= kilogramme degree }

It is the quantity of heat necessary to raise 1° C. the temperature of 1 kilogramme of distilled water.

Kilogrammetre = Kgm = the power necessary to raise 1 kilogramme, 1 metre high, in one second. It is equal to $\frac{1}{75}$ of a French horse power. An English horse power = 550 foot pounds, while a French horse power = 542.7 foot pounds.

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No. of units.	Inches to centimetres.	Feet to metres.	Yards to metres.	Miles to Kilometres.	Millimetres to inches.
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2	5.0799	0.6095890	1.82876696	3.2186	0.07874158
3	7.6199	0.9143835	2.74315044	4.8279	0.11811237
4	10.1598	1.2197680	3.65753392	6.4373	0.15748316
5	12.6998	1,5239724	4.57191740	8.0466	0.19685395
6	15.2397	1.8287669	5.48630088	9.6559	0.23622474
7	17.7797	2.1335614	6.40068436	11.2652	0.27559553
8	20.3196	2.4383559	7.31506784	12.8745	0.31496632
9	22.8596	2.7431504	8.22945132	14.4838	0.35433711
10	25.3995	3.0479450	9.14383480	16.0930	0.39370790

No. of units.	Centimetres to inches.	Metres to feet.	Metres to yards.	Kilometres to miles.	Square inches to square centimetres.
1	0.3937079	3.2808992	1.093633	0.6213824	6.45136
2	0.7874158	6.5617984	2.187266	1.2427648	12.90272
3	1.1811237	9.8426976	3.280899	1.8641472	19.35408
4	1.5748316	13 1235968	4.374532	2.4855296	25.80544
5	1.9685395	16.4044960	5.468165	3.1069120	32.25680
6	2.3622474	19.6853952	6.561798	3.7282944	38.70816
7	2.7559553	22.9662944	7.655431	4.3496768	45.15952
8	3.1496632	26.2471936	8.749064	4.9710592	51.61088
9	3.5433711	29.5280928	9.842697	5.5924416	58.06224
10	3.9370790	32.8089920	10.936330	6.2138240	64.51360

No. of units.	Square feet to sq. metres.	Sq. yards to sq. metres.	Acres to hectares.	Square centimetres to sq. inches.	Sq. metres to sq. feet.
1	0.0929	0.836097	0.404671	0.155	10.7643
2	0.1858	1.672194	0.809342	0.310	21.5286
3	0.2787	2.508291	1.204013	0.465	32.2929
4	0.3716	3.344388	1.618684	0.620	43.0572
5	0.4645	4.180485	2.023355	0.775	53.8215
6	0.5574	5.016582	2.428026	0.930	64.5858
7	0.6503	5.852679	2.832697	1.085	75.3501
8	0.7432	6.688776	3.237368	1.240	86.1144
9	0.8361	7.524873	3.642039	1.395	96.8787
10	0.9290	8.360970	4.046710	1.550	107.6430

No. of units.	Square metres to sq. yards.	Hectares to acres.	Cubic inches to cubic centimetres.	Cubic feet to cubic metres.	Cubic yards to cubic metres.
1	1.196033	2.471143	16.3855	0.02831	0.76451
2	2.392066	4.942286	32.7710	0.05662	1.52902
3	3.588099	7.413429	49.1565	0.08494	2.29354
4	4.784132	9.884572	65.5420	0.11325	3.05805
5	5.980165	12.355715	81.9275	0.14157	3.82257
6	7.176198	14.826858	98.3130	0.16988	4.58708
7	8.372231	17.298001	114.6985	0.19819	5.35159
8	9.568264	19.769144	131.0840	0.22651	6.11611
9	10.764297	22.240287	147.4695	0.25482	6.88062
10	11.960330	24.711430	163.8550	0.28315	7.64513

No. of units.	Cubic centimetres to cubic inches.	Litres to cubic inches.	Hectolitres to cubic feet.	Cubic metres to cubic feet.	Cubic metres to cubic yards.
1	0.06102	61.02705	3.5317	35.31659	1.30802
2	0.12205	122.05410	7.0634	70.63318	2.61604
3	0.18308	183.08115	10.5951	105.94977	3.92406
4	0.24411	244.10820	14.1268	141.26636	5.23208
5	0.30514	305.13525	17.6585	176.58295	6.54010
6	0.36617	366.16230	21.1902	211.89954	7.84812
7	0.42720	427.18935	24.7219	247.21613	9.15614
8	0.48823	488.21640	28.2536	282.53272	10.46416
9	0.54926	549.24345	31.7853	317.84931	11.77218
10	0.61027	610.27050	35.3166	353.16590	13.08020

No. of units.	Grains to grammes.	Ounces avoir. to grammes.	Ounces troy to grammes.	Pounds avoir. to kilogrammes.	Pounds troy to kilogrammes.
1	0.064773	28.3375	31.0913	0.4534148	0.373096
2	0.129546	56.6750	62.1826	0.9068296	0.746192
3	0.194319	85.0125	93.2739	1.3602444	1.119288
4	0.259092	113.3500	124.3652	1.8136592	1.492384
5	0.323865	141.6871	155.4565	2.2670740	1.865480
6	0.388638	170.0250	186.5478	2.7204888	2.238576
7	0.453411	198.3625	217.6391	3.1739036	2.611672
8	0.518184	226.7000	248.7304	3.6273184	2.984768
9	0.582957	255.0375	279.8217	4.0807332	3.357864
10	0.647730	283.3750	310.9130	4.5341480	3.730960

No. of units.	Long tons to tonnes of 1000 kilog.	Pounds per square inch to kilogrammes per square centimetre.	Grammes to grains.	Grammes to ounces avoir.	Grammes to ounces troy.
1	1.015649	0.0702774	15.438395	0.0352889	0.0321633
2	2.031298	0.1405548	30.876790	0.0705778	0.0643266
3	3.046947	0.2108322	46.315185	0.1058667	0.0964899
4	4.062596	0.2811096	61.753580	0.1411556	0.1286532
5	5.078245	0.3513870	77.191975	0.1764445	0.1608165
6	6.093894	0.4216644	92.630370	0.2117334	0.1929798
7	7.109543	0.4919418	108.068765	0.2470223	0.2251431
8	8.125192	0.5622192	123.507160	0.2823112	0.2573064
9	9.140841	0.6324966	138.945555	0.3176001	0.2894697
10	10.156490	0.7027740	154.383950	0.3528890	0.3216330

No. of units.	Kilogrammes to pounds avoirdupois.	Kilogrammes to pounds troy.	Metric tonnes of 1000 kilog. to long tons of 2240 pounds.	Kilog. per square millimetre to pounds per square inch.	Kilog. per square centimetre to pounds per square inch.
1	2.205486	2.6803	0.9845919	1422.52	14.22526
2	4.410972	5.3606	1.9691838	2845.05	28.45052
3	6.616458	8.0409	2.9537757	4267.57	42.67578
4	8.821944	10.7212	3.9383676	5690.10	56.90104
5	11.027430	13.4015	4.9229595	7112.63	71.12630
6	13.232916	16.0818	5.9075514	8535.15	85.35156
7	15.438402	18.7621	6.8921433	9957.68	99.57682
8	17.643888	21.4424	7.8767352	11380.20	113.80208
9	19.849374	24.1227	8.8613271	12802.73	128.02734
10	22.054860	26.8030	9.8459190	14225.26	142.25260

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