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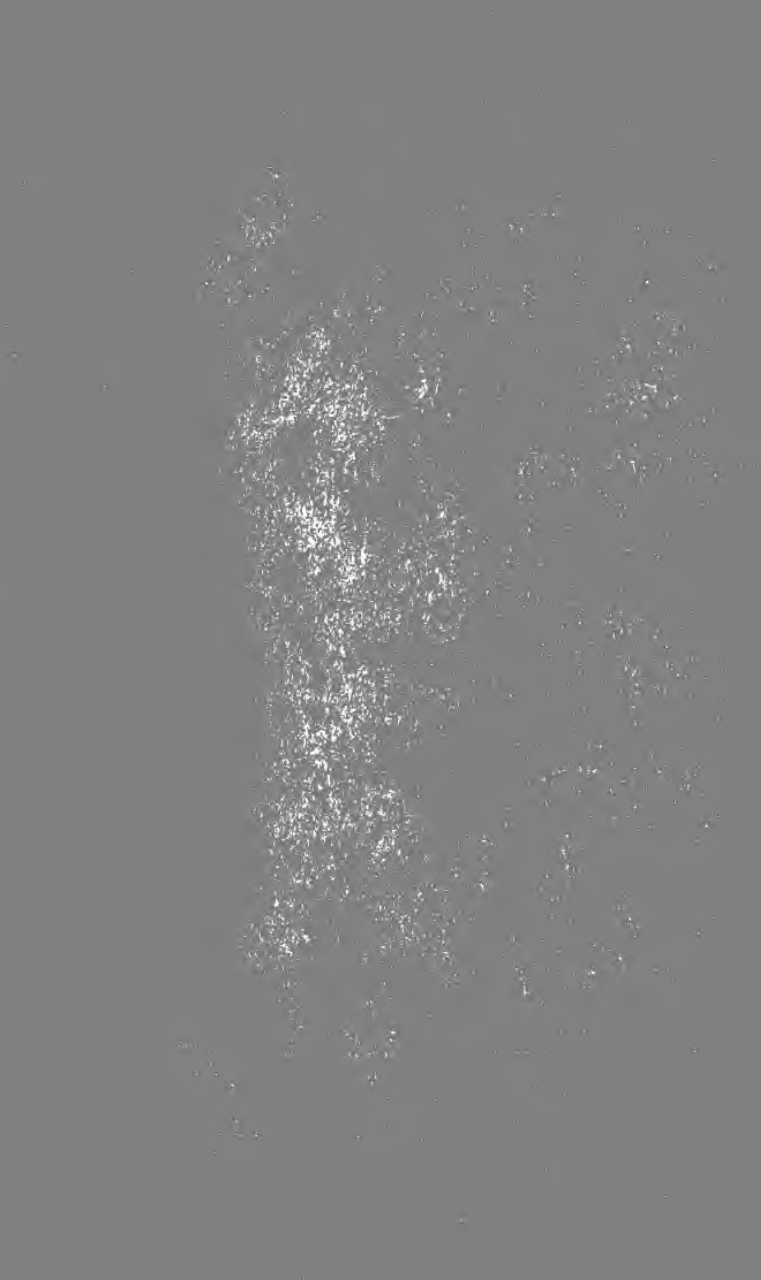
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PAINTERS'
COLOURS, OILS, AND VARNISHES:
A PRACTICAL MANUAL.

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PAINTERS'
COLOURS, OILS, AND VARNISHES:

A PRACTICAL MANUAL.

BY

GEORGE H. HURST, F.C.S.,

MEMBER OF THE SOCIETY OF CHEMICAL INDUSTRY;
LECTURER ON THE TECHNOLOGY OF PAINTERS' COLOURS, OILS, AND VARNISHES,
AT THE MUNICIPAL TECHNICAL SCHOOL, MANCHESTER.

With Numerous Illustrations.



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1892.

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P R E F A C E.

IN offering the following pages to Practical Workers and others interested in the wide subject of "Painters' Colours, Oils, and Varnishes," my aim throughout has been to combine theory and practice, and to show the scientific principles that underlie the methods in constant use. Naturally—and one may say unavoidably—there has grown up in the course of years, in connection with Colour-making, as with every other industry, a good deal of what is known as "Rule of thumb" procedure. The amount of this that prevails, however, has been greatly overrated, and we are not far distant from the day when "Rule of thumb" will be generally supplemented among us by an intelligent appreciation of the scientific principles involved. To give the *rationale* of every technical process is, nevertheless, by no means an easy task, and all that I can hope to have effected is the placing before the reader such a description of the various processes and their underlying principles, as shall be really helpful in practical work.

The information given as to the properties and preparation of Pigments, is either based on my own experience, or drawn from the most trustworthy sources. For a revision of the chapter on Varnishes, and many excellent suggestions, I am indebted to a personal friend, practically engaged in their

manufacture. My best thanks are due to him, and also to Messrs. Brinjes & Goodwin, Follows & Bate, Ritchie & Co., Rose, Downs & Thompson, and Rushton, Irving & Co., who have kindly furnished for the work illustrations of the newest types of Paint and Oil Machinery.

GEORGE H. HURST.

CHEMICAL LABORATORY,
22 BLACKFRIARS STREET,
MANCHESTER, *October, 1892.*



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PAINTERS' COLOURS, OILS, AND VARNISHES.

CHAPTER I.

INTRODUCTORY.

COLOUR, COLOURS, PAINTS, AND VARNISHES.

Colour is a term used by persons in several senses; hence confusion sometimes arises, although, as a rule, the context leaves no doubt as to the particular sense intended. When a beam of white light is made to pass through the angle of a triangular prism in a certain manner, and the light which has passed through is received upon a screen, we find that it has undergone a wonderful change; instead of being one uniform colour, as it was originally, it is spread out into a band of many colours, of which seven can readily be distinguished—viz., red, orange, yellow, green, blue, indigo, and violet. We see these colours by the effect or sensation produced by their action on the retina of the eye; in a sense, therefore, these colours have an abstract existence only, we can see them by the eye, but we cannot handle them as we can a piece of cotton. When we speak of a red colour or a green colour, we use the term "colour" in an abstract sense to indicate the sensation which these colours create in our eyes. On the other hand, we often speak of coloured bodies (that is bodies which give the sensation of being coloured when we look at them) as "colours," especially when (as with vermilion, chrome yellow, emerald green, Prussian blue, and magenta) they can be used to impart colour to other bodies. In this way "colour" is used in a concrete sense to indicate

tangible bodies which have the power of causing other bodies to which they may be applied to create, so to speak, the sensation of colour. Although the subject is one of some importance to users of colours, it is not intended to enter here into a long discussion of colour from an abstract point of view, inasmuch as space does not admit of doing so in any adequate manner, the reader must, therefore, be referred to other works specially devoted to the consideration of the subject.

The Spectrum-Colours.—When, then, a beam of white light is passed in a particular manner through the edge of a triangular prism, it undergoes two changes—(1) the direction of its course is altered, *i.e.*, it becomes refracted; and (2) the beam of white

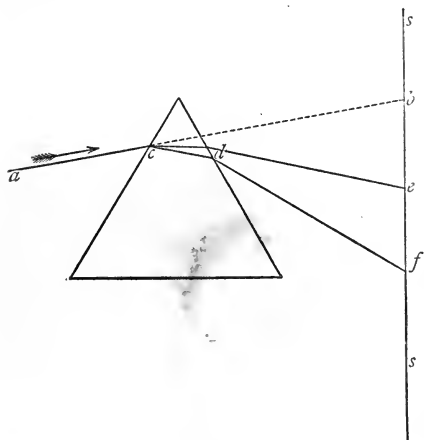


Fig. 1.

light is separated into a divergent band of several differently-coloured light-rays. Fig. 1 represents the path of a beam of light through a triangular prism; *a* is a ray travelling in the direction of the arrow which strikes the prism at *c*. If the prism had not been there, it would have passed on and would have fallen upon the screen, *s, s*, at *b*; but the prism, bending it out of this course, refracts it as shown at *c*; it then passes through the prism in the new direction until it

emerges at *d*, where it is again refracted so as to take the new direction, *d, f*. As the amount of refraction differs for each ray according to its colour, the result is that the original white beam of light is differentiated into a long band of numerous distinct colours, known as the *spectrum*, which extends from *e* to *f* in the screen. The rainbow is a spectrum of this kind formed by the refraction of the sun's light during its passage through the drops of water in a shower of rain. In the latter case, however, the spectrum is seen in front of the drops, not behind them, as it is formed by the rays, which, falling on the drops, pass to the back, and are then reflected so as to emerge again on the side nearest the sun.

The colours of the spectrum are pure colours—*i.e.*, they cannot be further split up; if, say, the red part of the spectrum be passed through a second prism, no new colours are produced; the light which passes through the second prism is still red, although it is distributed over a wider surface. It, therefore, follows that there are really a very large number of simple colours in the spectrum, although, owing to the limitations of language, it is impossible to separate and name every one of these in a popular manner; although scientists can do so in another manner which it is not necessary to describe here. It is, however, customary to follow the lead of Sir Isaac Newton, who discovered this property of white light, and to distinguish seven colours—*viz.*, red, orange, yellow, green, blue, indigo, and violet; but it should be distinctly understood that in the spectrum there is no well-marked line of division between these seven so-called primary colours; the red passes insensibly into the orange, the orange into the yellow, and so on through the other colours in the order given above.

White from Coloured Light.—By passing the spectrum colours through a lens, or through another prism, in a particular manner, the seven colours can be recombined so as to form white light. It is not even necessary to use all the spectrum colours, as two or three will suffice if properly selected. Thus blue and yellow will when united form white light; as also red, green, and blue, and many other combinations, particulars of which will be found in special books on Colour, such as those of Professor Church and Mr. W. Benson. The consideration of this property of a few of the spectrum colours combining together to form white light led Young, and, later, Helmholtz, to consider that there are only three primary colours, red, green, and blue, from which all the other colours can be obtained; thus, by combining red and green, yellow is produced; or by combining red and blue violet is the result.

Light from Coloured Bodies.—When the light which is reflected from the surface of a coloured body like vermilion is passed through a prism, it is found to yield a spectrum; not, however, a complete one, such as is got from a ray of white light, but one more or less incomplete; thus, vermilion gives a spectrum containing some red, orange, and a little blue light; chrome yellow again gives a spectrum showing a few red, some yellow, and some green rays; in each case the eye distinguishes the effect due to the combined action of all these rays on the retina. No artificial colouring-matter is known which reflects rays of one colour only; in every case the rays of the dominant colour are mingled with those of other colours. The light from some bodies

is of a very complex character, while that from others is comparatively simple. It is this complexity in the composition of the light reflected that makes it so difficult to demonstrate the true laws and facts of colour with pigments or any artificial colouring-matters.

Cause of Colour in Coloured Bodies.—The actual reasons why bodies such as vermilion, magenta, or emerald green are coloured, it is almost impossible to investigate in the present state of knowledge, since the cause, whatever it may be, must be due to the molecular construction of the different compounds about which very little is known; still, we know something of some of the reasons why coloured bodies appear coloured. When light falls upon a substance, the light may be affected in one or two ways; it may be reflected, that is, it may be thrown back from the body; or it may be transmitted, that is, it may pass through, or, in some cases, be absorbed by the body on which it has fallen. As a rule, there is never either complete reflection or complete transmission of light, the most perfectly reflecting body allowing some rays to pass into it. It is by reflected light that we see bodies; when the reflection is complete, or as nearly so as is the case with mercury or a very highly polished plate of silver, the body is nearly invisible; it is only rendered visible because it does not reflect all the light which falls upon it in a regular manner; some is irregularly reflected and it is this light which enables us to see the body. Two kinds of reflection can, therefore, be distinguished—regular and irregular. Regular reflection is that where the light is thrown back in a straight line from the reflecting surface; if this is perfect, only the light that is reflected is seen, the reflector itself is invisible. Irregular reflection is that where the light is thrown back from the reflector in every direction; it is this light which makes the body visible, and it is due to the fact that no matter how apparently even the surface may appear to be, yet it is not even; it is sufficiently rough to cause the light which falls upon it to be irregularly reflected. Then bodies never reflect or absorb the whole of the light which falls upon them, some of it is absorbed; the most perfectly polished plate of silver (which is the most highly reflecting body known) does not reflect the whole of the light which falls upon it, while a piece of black cloth reflects only a little of the light that falls upon it. Upon the character of the reflected light thrown off from a body depends its colour, which is independent of the proportion of the light that falls upon and is reflected by the body. If all the rays of light falling upon it are reflected, then the body appears white; if all the light rays are absorbed, then the body

appears to be black. If, now, some of the spectral rays are absorbed and the rest reflected, then the body appears to be coloured, the colour depending upon the composition of the rays which are reflected; thus the rays from a red body, such as vermilion, are red, as are also those from Derby red and oxide of iron; similarly, the rays from a yellow body, such as chrome yellow or yellow ochre, are yellow, but it does not follow that the rays from all red bodies or from all yellow bodies are identical in composition. If the rays from, say, vermilion, oxide of iron, and crimson lake are passed through a prism, and the spectra of the coloured light which is reflected from each examined, they will be found to be different; that from the crimson lake will contain more blue rays than that from the vermilion, while that from the oxide of iron will contain more of the dark red and indigo rays than either of the others; and it is the same with the other classes of colours. There is no coloured body known which reflects what might be called a pure light, while the spectrum-colours are pure, as has been already stated. It is this compound nature of the light which is reflected from coloured bodies that makes it extremely difficult to demonstrate the true laws of light and colour by the use of pigments.

In the same manner as the coloured light which is reflected from bodies is compound, so that which is transmitted is compound and, usually, the complement of that which is reflected, but this does not always happen. When it is the complement of that which is reflected, then the bodies which give rise to this phenomena are known as dichroic; in other cases both the reflected and transmitted rays are of the same general colour, although there is usually some difference in the actual tint of the two colours.

It is assumed that the coloured bodies have a selective action on the light which falls upon them, reflecting or transmitting, as the case may be, those coloured rays to which they owe their colour, while they absorb all the other rays. White bodies reflect all the rays which fall upon them, black bodies absorb all and are, in consequence, often nearly invisible. As to the character of the rays reflected from red, orange, yellow, green, or other coloured bodies, these will have been inferred from what has been said above.

Colour Theories.—Two theories of colour are in use to explain the coloured effects of light. The old theory, which is mostly due to Brewster, considers that there are three primary colours—viz., red, yellow, and blue; by the proper admixture of which in various proportions all the other colours can be

obtained. The more modern theory, first broached by Young and more fully developed by Helmholtz, considers that there are three primary colours, red, green, and blue, although some authorities add a fourth. However, it must be confessed that while the modern theory accurately explains all the phenomena of colour producible by the use of the spectrum colours, yet the older theory of Brewster more easily explains the phenomena of colour as produced by the admixture of the various colouring-matters, pigments, and dyestuffs in common use; this arises not from any fault in the newer theory, but from the compound nature of the light which is reflected or transmitted from the colouring-matters in question. Of the newer theory it is not intended to deal, although it is advisable for colourists to make themselves acquainted with it; as to the old theory, it will be sufficient to say that when any two of the primary colours are mixed together a so-called secondary colour is produced; thus red and yellow produce orange, red and blue produce violet, while yellow and blue make green. When the secondaries are mixed together they produce what are called tertiary colours, of which there are six, known as buff, citrine, sage, slate, plum, and russet. The nomenclature of these tertiary colours is very indefinite, and different authorities give them different names.

The common theory of red, blue, and yellow is not wholly satisfactory, as it does not account for all the shades which may be produced by the admixture of pigments; thus a mixture of ultramarine, a blue, with yellow ochre, a yellow, does not produce a green, as the theory would expect, but a kind of greenish-grey; this effect can, however, be explained by the blue-red-green theory when we know the kind of rays reflected by the two pigments in question. Reference must be made to text-books on colour for a further development of the subject.

Colours.—It has been explained above that the term “colours” is used in two senses—first, to express the sensation which light of various kinds evolved from bodies excites on the retina of the eye, and which sensation is purely functional; second, to denote those bodies which, having the property of selective absorption of coloured rays from the light which falls upon them, appear to be coloured and which have the property of imparting this colour to other bodies; such bodies are known as colouring matters and may be divided into two groups, dyestuffs and pigments; the former are mostly soluble in water and are used solely to dye cotton, wool, or other textile fibres, while the latter are insoluble, and are used in the preparation of paints.

Besides these two classes of coloured bodies there is another group which are distinguished by the fact that while possessing colour yet they cannot impart this colour to other bodies ; such are bluestone (sulphate of copper), nitrate of cobalt, chrome alum, &c.

Pigments.—These are a fairly numerous class of colouring matters which are used to give colour to paint. They are mostly derived from the mineral kingdom, although a few are obtained from organic sources. As a class they are distinguished by being insoluble in water, turpentine, and most other solvents with the exception of the strong acids ; they are opaque or nearly so ; and they should be perfectly inert bodies exercising no action of any kind on any other substance with which they may be mixed. As typical examples of pigments may be taken barytes, oxide of iron, yellow ochre, chrome green, and umber.

In dealing with pigments in detail they will, as a rule, be considered under the divisions of white pigments, red pigments, yellow pigments, and so on ; but here and there, deviations from this rule will be made, as in the case of Derby red (which will be dealt with under the head of yellow pigments) and in the case of lakes, where it is thought that the composition and properties of the particular pigments can be more conveniently pointed out, if dealt with in one group.

Paint.—Paint is the name given to a liquid composition which is used very extensively for two purposes—first, to act as a protective substance to preserve the body on which it has been applied from the destructive action of the weather ; second, as a decorative agent.

The first object is brought about by making the paint with materials which are not acted upon by the various agents present in the atmosphere, such as water, acid vapours, light, oxygen, that exert a more or less destructive action on bodies which may be exposed to their action. The bodies which have been found to resist this destructive action of the atmospheric influences are the various so-called drying oils, resinous matters, and the pigments. A paint is a liquid composition which will remain liquid until it is applied to the body to be painted, and yet when so applied and afterwards exposed to the atmosphere will dry and leave behind it a firm, hard (yet elastic), and opaque coating, which may be more or less lustrous and be capable of resisting the weather. The opacity of the coating is obtained by using pigments of various kinds, which also tend to increase the resisting power of the paint, and these pigments are mixed with liquid bodies, such as oils and spirits, which are

used partly to obtain a composition that is easy of application, and partly to secure volatility, so that when alone or when mixed with resinous matters, they will evaporate away and leave behind a hard mass firmly binding the pigments to the body over which they have been painted. The liquid bodies which have been found to answer this purpose best are the drying oils, such as linseed oil, which when spread over a surface and exposed to the air absorb oxygen and dry into a hard mass; but as these oils, for various reasons (which will be more fully dealt with later on), cannot be used alone with satisfactory results it becomes necessary to mix them with some solvent, such as turpentine or shale naphtha, which is volatile. In some kinds of paints a little resinous matter is used, which dissolves in the solvent; on exposure the latter evaporates off, leaving the resin behind in the form of a dry coat on the surface to which it has been applied. Paint is always more or less coloured to add to the decorative effect. Its primary purpose, however, is to hide the character of the surface to which it is applied and, as has been pointed out, to protect this surface.

Varnishes.—These bodies are very similar to paints in their properties and uses. They differ in giving a transparent lustrous coat of a very resistant character to the destructive action of the weather. They may be coloured; but, if so, transparent colours are used and not, as in the case of paints, opaque pigments. They are composed of a resinous matter dissolved in various oils and solvents, the latter forming the vehicle by means of which the resin is transferred to the surface to be varnished. The special properties of varnishes will be dealt with later on.

CHAPTER II.

WHITE PIGMENTS.

THE white pigments are a very important group of painters' "colours," probably the most important, as while the red, blue, green, &c., pigments are used simply or almost entirely as colouring pigments, the white pigments are used in two ways—1st, as "body colours," *i.e.*, to give body or covering power to paint; 2nd, as "colouring pigments." Thus, in making a red paint, white lead or barytes is added to give the necessary body and vermilionette is used to colour the paint. On account of this dual feature of the white pigments they merit a more detailed account of each individual member of the group than is necessary for other pigments.

The white pigments are a fairly numerous group of bodies derived entirely from inorganic sources. Many white bodies are known which could be used as pigments, but are not so used on account of expense, &c. The following list comprises all that are used either on a large or small scale:—

White Lead, basic carbonate of lead, $2 \text{PbCO}_3 \cdot \text{PbH}_2\text{O}_2$; this pigment is also sold under a variety of other names.

Lead Sulphate, PbSO_4 ; many pigments sold under various fancy names consist essentially of this body combined with other white pigments.

Lead Oxychloride, Pb_2OCl_2 , Pattinson's white lead.

Zinc White, zinc oxide, ZnO .

Zinc Sulphide, ZnS ; this body combined with barytes, &c., is largely used as a white pigment.

Barium Sulphate, BaSO_4 , barytes.

Barium Carbonate, BaCO_3 .

Calcium Sulphate, CaSO_4 , gypsum.

Calcium Carbonate, CaCO_3 , whiting.

Calcium Oxide, CaO , quicklime.

Strontium Sulphate, SrSO_4 .

Strontium Carbonate, SrCO_3 .

Magnesium Carbonate, MgCO_3 , magnesite.

China Clay, hydrated silicate of alumina.

French Chalk, silicate of magnesia.

Of these, the most important are white lead, lead sulphate, zinc white, zinc sulphide, barytes, gypsum, calcium carbonate, and china clay.

WHITE LEAD.

White lead has been known and used as a pigment for centuries; the Romans and Greeks used the native carbonate of lead or "cerusse," as it was then called, from which the mineralogical name cerussite has arisen. This natural pigment is found only in comparatively small quantities, and it is no wonder that a process for the artificial production of white lead was soon found out and adopted, with the result that natural cerussite is not now used as a pigment.

It is not known when white lead was first made, who made it, or to what country it owes its birth. The oldest known method is that commonly called the "Dutch method," from the supposition that it was invented in Holland; it is described as the Dutch process in an English patent granted in 1787, and there is no doubt but that it is the process referred to in three earlier patents granted in 1622, 1635, and 1745, in which it is spoken of as an old process. Evidently white lead has been made for several centuries. During all this period there has been but little change made in the Dutch process. But in the interval inventors have not been idle, for there is no other pigment which has attracted so much attention at their hands as white lead; and the number of processes and modifications of processes which have been devised, is almost innumerable. With all this invention, the ancient Dutch process still retains its pre-eminence as the best process for the manufacture of white lead.

MANUFACTURE OF WHITE LEAD.

White lead, the basic carbonate of lead, is manufactured by a variety of methods. It is not easy to classify these processes into groups, as they not unfrequently pass one into the other imperceptibly. The author suggests the following classification, which is based on the principles which appear to underlie the various methods adopted, or which have been proposed and used on a limited scale:—

1st Group.—Stack method.

2nd Group.—Chamber methods.

3rd Group.—Precipitation processes based on the action of carbonic acid gas on various lead salts.

4th Group.—Precipitation methods based on the action of alkaline carbonates on various lead salts.

5th Group.—Miscellaneous methods. Most of these are now obsolete and are only of historical interest.

1st GROUP.—STACK METHOD.

Only one process is included in this group, the old Dutch or stack process. No process which is now in use or which has been proposed can claim the antiquity that this process can, and, notwithstanding all the labours of chemists and white lead

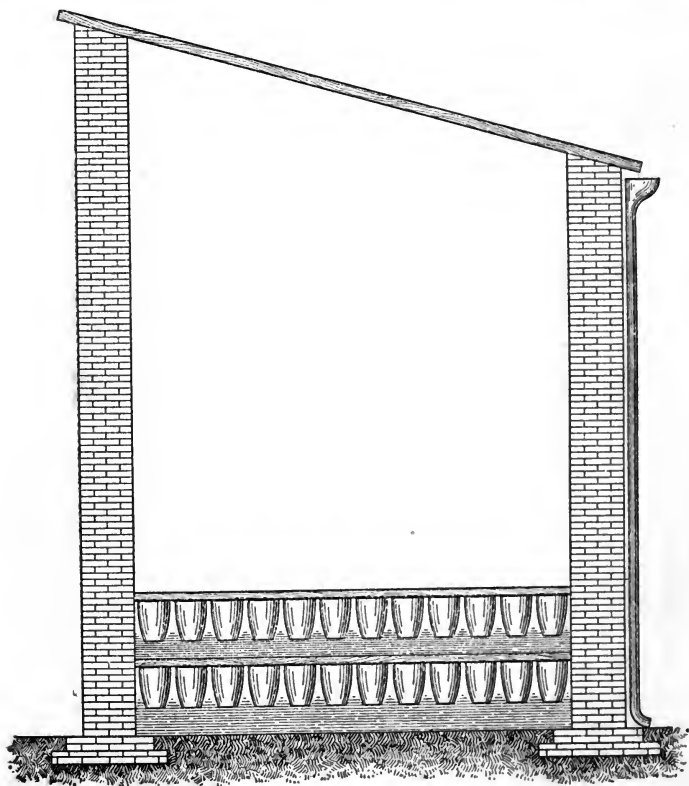


Fig. 2.—Shed for making white lead.

makers to supersede it, for reasons which will be pointed out presently, it still remains the best process for the manufacture of white lead. Tradition assigns its discovery to the Dutch and to a person named Stratingh in particular. It must be at least 300 years old. Since 1787 this process has been carried on without much alteration in its details. The Dutch method is used in all

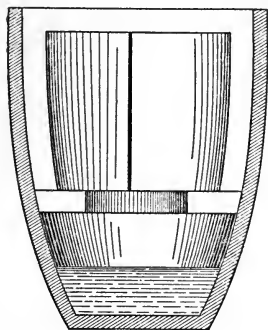


Fig. 3.

parts of the world for the manufacture of white lead, and there is but little variation in the details of the process and in the construction of the plant used in different countries.

The plant used in the stack process is shown in Figs. 2 to 5. A shed of brickwork, Fig. 2, is built, the size of which varies a little, but averages 16 feet long by 13 feet wide and 20 feet high; this may have either a lean-to roof, as shown in the figure; or, as in some works, two of these sheds are built back to back, with a single-ridge roof between them.

In some places parts of the structure are built below the level of the ground, but there is no advantage to be gained by so doing: A large white-lead works will have a number of these sheds, so as to keep the workmen fully occupied with filling and emptying them.

A number of earthenware pots are provided. These pots vary in size at different works, but an average size is 8 inches high by

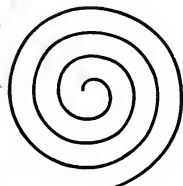


Fig. 4.

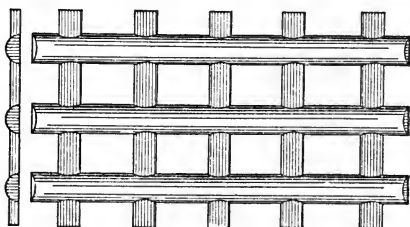


Fig. 5.

4 inches in diameter. In shape they resemble crucibles (see Fig. 3), but have a shelf inside, as shown. In the bottom of these pots is placed some weak acetic acid or vinegar; this diluted acid contains about 2 to 3 per cent. of actual acetic acid. On the shelf inside the pot is placed a roll of thin sheet lead (Fig. 4),

made from a strip of lead 2 feet long by $4\frac{1}{2}$ inches broad. In a stack of ordinary dimensions some 11,000 to 12,000 of these pots will be used, and they will contain about 800 to 900 gallons of weak acid.

The stack is built up as follows:—First, a layer of ashes, upon which is placed a layer of spent tan of about 3 feet in thickness. In the older Dutch method horse-dung was used, but this is open to some disadvantages which will be pointed out presently; the use of tan was introduced in England so that this modification of the Dutch process is sometimes spoken of as the English method. This layer of tan is pressed down very firmly and is evenly spread; on it is placed a layer of the pots, which layer is kept at a distance of about 6 inches from the sides of the shed. In some works the outside rows of pots are made of larger size than the others, so as to act as supports for a layer of flooring boards. In other places the pots are all of one size and wooden supports for the boards are provided.

On the top of the pots is placed a layer of lead buckles or gratings (Fig. 5). These are placed face to face in a layer of about 3 to 5 inches thick; above these comes the layer of flooring boards, a space of about 6 inches being left between them. On the top of the boards another layer of tan, then a layer of pots, then a layer of gratings, then another layer of boards, and so on until the stack is completely built up. The number of sets of layers varies from seven to eleven. The doorway through which the filling is done is closed as the work progresses by boarding, but a small space is left at the top through which the progress of the operation can be observed, and fresh additions of material made as required to allow for sinking of the tan, &c.

The quantity of lead used varies considerably, or from about 3 tons to 7 tons in a layer of materials, so that in a large stack there may be something like 85 tons of lead.

In stacks of very large area it is usual to construct chimneys throughout the mass, whereby the steam which is produced during the operation is carried off; in stacks of small area, these chimneys are not required, as the space around the side walls of the shed affords a sufficient outlet.

When the stack is built up it is left for a period of about three months. During this period the stack gets quite hot (140° F.) through the fermentation of the tan which sets in; large quantities of carbonic acid gas are given off, and the acetic acid is converted into vapour. The "blue lead" is gradually converted into "white lead." At the end of three months the stack is pulled to pieces. As the boards are removed it is found

that the lead which has been corroded still retains the form of the blue lead, but is more bulky in volume, is white or greyish in tint, and opaque. The corrosions are not of a uniform character throughout the whole of the stack; in some places they are porcellaneous and flaky, are firm to handle, do not break up, and give the best quality of white lead; in other parts of the stack the corrosions are soft, easily crumble to a fine powder or dust when handled, and do not give a good quality of white lead. In some places the lead may be discoloured owing to a variety of causes, such as the presence of tarry matter in the acid (especially when crude pyroligneous acid is used), by droppings of coloured water from the layer of tan on to the lead, &c. In chemical composition the corrosions will vary; in some places they will approximate closely to the normal composition of white lead, 2Pb C O_3 , $\text{Pb H}_2 \text{O}_2$, in others more nearly to that of 3Pb C O_3 , $\text{Pb H}_2 \text{O}_2$, while in others they consist of the normal carbonate, Pb C O_3 .

As the stack is being pulled to pieces the corrosions are carried to the grinding rooms. The method of treating the white lead varies in different works, but the following may be taken as a good example of the usual manner of working:—The corrosions are first passed through a pair of rolls; these break up the masses, the white lead crumbles to powder, while the unchanged blue lead is flattened out into thin sheets. The crushed materials are then sieved, which separates the white from the blue lead; the latter is sent to the melting pot where it is melted and re-cast for use in building another stack. The white lead is sent into tanks full of water, where it is thoroughly agitated, and the small traces of acetate of lead which the corroded lead contains washed out of it. While still wet the white lead is ground as fine as possible under edge runners or between rollers, and then dried, when it is ready for sale. As the grinding must be thorough, the lead is passed through several sets of grinding mills.

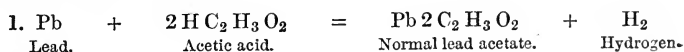
Grinding white lead is a source of danger to the workpeople, for the fine dust flies about the room in which it is done and is breathed by the workpeople, who, sooner or later, suffer from lead poisoning; much of this danger is avoided by grinding the lead in a wet condition only, when the particles of lead are practically too heavy to fly about.

The greatest risk now arises in the packing of the ground lead, as the workmen frequently get some on their hands and eat their meals without previously washing their hands. Lead poisoning may be prevented by drinking water acidulated with

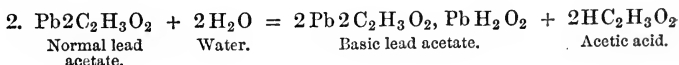
sulphuric acid, whereby the lead absorbed into the system is converted into the harmless sulphate of lead. The great trouble is that the workmen will not take sufficient care to make use of these precautions.

It was stated above that in the early or Dutch modification of this process, horse-dung was used as the source of the heat and carbonic acid necessary to carry on the process; while with dung the process is quicker (only taking from 8 to 9 weeks), yet it is not so good as the English method with tan, the product is not quite so regular in composition, and it is more liable to discolouration owing to the evolution of sulphuretted hydrogen from the decomposing dung, and to its combination with lead to form the objectionable black sulphide.

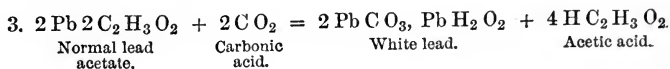
The theory of the process of white-lead making by the Dutch process, which at present is most favoured by chemists, and was substantiated by some experiments carried out by Hochstetter, is due to Liebig. The first action which goes on in the stack is to convert the blue lead into basic acetate of lead; this is brought about by the heat of the fermenting tan, or dung, causing the evolution of acetic acid from the liquid in the pots, which, attacking the lead, causes the production of the normal acetate of lead, thus—



The normal lead acetate, under the influence of water and heat, parts with some of its acetic acid and passes into the basic acetate, thus—

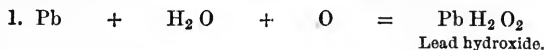


The acetic acid is ready to attack a further quantity of blue lead. The basic acetate is now attacked by the carbonic acid evolved by the fermenting tan, the acetic acid it contains is liberated and its place taken by the carbonic acid, and white lead is formed, thus—

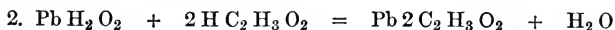


Although the reactions shown in the above equations are those usually accepted as representing the formation of white lead from blue lead in the stack process, yet they are probably

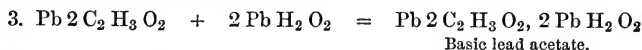
not quite correct ; the evolution of hydrogen in the first step in the process is rather improbable ; a better explanation would be the following :—(1) By the action of moisture and oxygen on the lead there is formed lead hydroxide, thus—



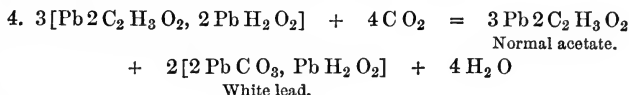
Then this being acted on by the acetic acid forms the normal or neutral acetate and water, thus—



The normal acetate now combines with lead hydroxide to form basic lead acetate, thus—



This is now acted upon by the carbonic acid with the formation of white lead and normal acetate, thus—



The normal acetate thus reproduced then forms more tribasic acetate by the reaction shown in equation 3. It is again decomposed by the carbonic acid, as shown in equation 4, so that a continuous cycle of changes is set up ; the lead being oxidised to lead hydroxide, and this converted into white lead, the basic carbonate, *pari passu* with its formation.

As a rule, nearly all the blue lead is converted into white lead, one ton of lead producing one and a quarter ton of white lead, the amount varying from time to time according to the degree of perfection with which the corrosion has proceeded.

The great fault of the Dutch process is the great length of time required (8 to 12 weeks), the great amount of capital it takes to construct a stack of lead, and the loss of interest which takes place on the capital while the lead is in process of making. Then there is always a risk, owing to some defect, of producing a useless and imperfectly corroded lead, which has to be sent to the smelting furnace and again reduced to blue lead. Hence it is that inventors have turned their attention to devising other methods of producing white lead which shall be free from the defects of the Dutch process ; so far, however, no such method has been discovered.

White lead, as made by the process described above, is a basic carbonate of lead having the composition

Lead carbonate, Pb C O_3 ,	68.95 per cent.
Lead hydroxide, $\text{Pb H}_2 \text{ O}_2$,	31.05 ,,
	<hr/>
	100.00 ,,
Lead monoxide, Pb O ,	86.32 per cent.
Carbonic acid, C O_2 ,	11.36 ,,
Water, $\text{H}_2 \text{ O}$,	2.32 ,,
	<hr/>
	100.00 ,,

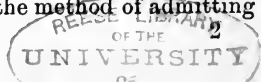
therefore having the formula $2 \text{ Pb C O}_3, \text{ Pb H}_2 \text{ O}_2$.

As will be seen hereafter, when the properties of white lead as a pigment come to be more fully considered, the carbonate is the substance to which white lead owes its colour and body; while the hydroxide with which it is associated, by chemically combining with the oil used to convert the white lead into a paint, imparts to the white lead great covering properties.

Numerous samples of white lead, of both high and low qualities, have been analysed by many chemists, some of which will be given later on. These analyses show that when the composition of any sample varies greatly from the figures above given, it is more or less defective. Generally, an increased proportion of carbonate, while causing the colour to be better, reduces the covering power; on the other hand, an increase in the amount of the hydroxide causes a loss of body and opacity. If the sample contain any monoxide then the tint becomes more yellow or greyish. Some of these points will be touched upon when considering the other processes for the production of white lead. In the meantime the success or non-success of any process depends upon the approximation of the white lead produced to the composition above given.

2nd GROUP.—CHAMBER METHODS.

In one sense the Dutch method just described is a chamber method, but it has been classed as a separate group because while being made in a chamber, it differs materially from those now to be described. In these processes the operation of white-lead making is carried on in large chambers in which metallic lead is placed, and into which currents of carbonic acid gas, acetic or other acid vapours, are passed, together with air and steam. The different methods are distinguished one from another by the construction of the chambers, the method of admitting the



acid gases, &c., and in other points. Although many such have been invented and will be found described in the Patent Records, yet very few are in actual operation for the production of white lead; and of those which have become obsolete very little is known beyond the, often very scanty, description which is to be found in the specification of the patent which protected the process.

In all the accounts which have appeared describing these processes, and which are evidently copied from one source, the chamber process is given as "the German method;" but it is a matter of doubt whether the process was invented in Germany or not. The author is inclined to consider it to be of English origin, partly because it is described in a patent taken out in 1749 by Sir James Creed, who makes no mention of having taken it from a foreign source. This was the first patent to describe a chamber process, and since then many have been patented; but the author must refer readers to the Patent Records for an account of these or to a series of articles which appeared in *The Chemical Trade Journal* in October and November, 1890.

1. Creed or German Process.—This process was the first in which chambers were used in conjunction with lead and acid gases. In detail it is carried out as follows:—A chamber of brickwork is built of any convenient size and with few openings, the usual ones are a door to enter into the chamber for the purpose of filling it, and an opening in the roof for ventilation; sometimes a window or two for the purpose of observation is added. The chamber has a number of shelves, on which are placed sheets or gratings of lead; it is immaterial which are adopted, although the gratings expose more surface to the action of the various gases which are used. When all the lead is placed on the shelves, the doors are closed, and currents of aqueous vapour, air, carbonic acid, and acetic acid at once admitted into the chamber. After a period varying from four to five weeks, the white lead will have been formed; it is collected and treated as in the Dutch process. The chemical action which proceeds is supposed to be the same as that which takes place in the old stack method. The acetic acid acts upon the lead, forming neutral acetate of lead; this, under the action of the aqueous vapour, is transformed into basic acetate of lead, and this, in its turn, is changed by the carbonic acid into basic carbonate of lead or white lead.

The quality of the product is usually very good, not, perhaps, quite equal to that produced by the Dutch method, but better than that produced by the precipitation processes. It is, how-

ever, inclined to be very variable, and the process requires some experience to carry out in the best possible manner to ensure a good product. It is desirable, as far as possible, to cause the white lead to approximate in composition to the formula 2Pb C O_3 , $\text{Pb H}_2 \text{ O}_2$, and to do this it is necessary that the gases should be sent into the chamber in the proper proportions. If excess of acetic acid is present, too much acetate of lead is formed, which is not decomposed by the aqueous vapour and the carbonic acid; too much of the latter tends to cause the formation of an excess of lead carbonate, and the white lead loses its covering powers. On the other hand, too much steam will lead to the formation of oxide, especially if the temperature be allowed to get high; the oxide so formed being of a yellow tint spoils the colour of the white lead. The same result is brought about by a deficiency of acetic acid. Experience is the only factor which can guide the white-lead maker in adjusting the various gases in the proper proportions.

The following are some analyses of white leads made by this process quoted by Weise:—

	1.	2.	3.	4.	5.
Lead monoxide,	86·80	86·24	86·03	84·69	83·47
Carbonic acid,	11·16	11·68	12·28	14·10	16·15
Water,	2·00	1·61	1·68	0·93	0·25

1. Firsts, of the best quality; good both in colour and body.
2. Seconds, not so good as No. 1, but still very serviceable as a pigment.
3. Thirds is only just usable as a pigment.
4. Is not usable except for very common purposes.
5. Not usable at all; it contains too much carbonate, and is sent to the smelting furnace.

Various alterations in the details of this method have been made from time to time by various inventors, some of which may be briefly noted. *Burton* placed the lead in coils on the shelves of the chamber, and passed the current of steam through perforated pipes, thereby converting the lead into oxide; when a sufficient amount of this has been formed the current of steam is stopped, and a current of acetic acid vapour sent in; this, acting on the basic acetate converts it into the basic acetate; when this action is finished the acetic acid current is stopped, and carbonic acid gas sent in, which acts on the basic acetate and changes it into basic carbonate or white lead. These currents of steam, acetic acid vapour, and carbonic acid gas are sent in successively until all the lead is converted into white lead, then the currents are

stopped, and the white lead is collected and finished in the usual way.

In *Richardson's method* the lead is soaked in a solution of acetate of lead, the action, both of the acetate and the gaseous bodies, to which the soaked lead is subjected being facilitated by the lead being cast into a granular form. After being soaked, the lead is placed on shelves in the chamber, and then subjected to the combined action of steam and carbonic acid gas, the chamber being maintained at a temperature of about 100° F.; the process is continued until all the lead is converted into white lead.

2. **Hatfield Process.**—This process resembles those just described to some extent, but differs in a few minor particulars.

The chamber is built with a double wall, and the bottom is hopper-shaped. The lead is cast into gratings of the same shape as used in the Dutch process, and placed in trays on shelves in the chamber. Into the chamber is sent water and acetic acid in the form of spray, at the same time the chamber is maintained at a suitable temperature by means of steam pipes. The action of the water and acid is to convert the lead into basic acetate of lead; when this has been properly formed the water and acetic acid spray is stopped, and a current of carbonic acid gas sent in to form white lead as described above.

3. **Thompson's method**, patented in 1873 and 1877, was worked by the Innocuous White Lead Co., of London. In this process the chamber is built of brick, with a large door and one or two windows, so that the progress of the operation can be observed. The bottom of the chamber is made like a trough and acid proof, glass being recommended as a material for its construction. The roof is built double, so that any liquid which is condensed will flow down to the sides and not drop on to the corroded lead below. The lead used is cast into gratings which are placed on open trucks fitted with shelves; the lead is soaked in a solution of acetate of lead and then wheeled into the chamber. A quantity of acetic acid is placed in the bottom of the chamber and vapourised by means of steam pipes passing through it, by which means the lead is converted into the basic acetate; when this action is complete, carbonic acid gas is sent in to change it into white lead. This was said to be of good quality. In the practical application of this process, much depends upon the temperature at which the chamber is maintained during the operation. If too high, then there is a tendency to form oxide of lead which does not readily change into white lead; if too low, then the action of the acid on the

lead is not energetic enough ; if too much acetic acid is used, then the tendency is to form normal acetate of lead which reduces the yield of white lead, and at the same time tends to cause this to have too much carbonate in its composition.

A very similar process to this was patented by *Morris*. In this the lead was used in the form of sponge or wire so as to expose as much surface as possible to the action of the various gases. The acetic acid was placed in vessels on the floor of the chamber and steam and carbonic acid gas passed in, a constant current of these gases being maintained. The white lead was gradually formed, and when complete was collected and finished in the usual way.

4. **Gardner's Electric Process.**—In 1882, Prof. E. V. Gardner patented a process for making white lead which, as he considers that electricity plays a part, he calls an “electric process.”

The specification of this patent (No. 731, of 1882) is very full, and is well worth reading by white-lead makers. In the specification the conditions most favourable to a successful production of white lead are fully stated, and from it the following is abstracted :—

As has been previously pointed out, in making white lead by the chamber methods there are several factors which require attention, if the product is to be a good one. Prof. Gardner states these to be as follows :—The proper formation of what he calls the sub-acetate or sub-nitrate of lead ; these basic salts are the compounds of the normal salts with the hydroxide of lead, and, therefore, have the formulæ $Pb\ 2\ C_2\ H_3\ O_2$, $Pb\ H_2\ O_2$ for the sub-acetate, and $Pb\ 2\ N\ O_3$, $Pb\ H_2\ O_2$ for the sub-nitrate. It is usual to consider the so-called subsalts of lead as compounds of the normal salts with the monoxide ; probably both kinds of salts exist—that is, there are compounds both of the monoxide and of the hydroxide of lead with the normal salts of lead. In white-lead making it is reasonable to suppose that better results would be obtained if the hydroxide compounds were formed than if the monoxide compounds were obtained in the process of making. Hence the conditions most favourable for the formation of the hydroxide should be carefully ascertained.

Temperature is an important factor ; this should be from 120° to 130° F. A lower temperature increases the length of time required for the formation of the subsalts, and so increases the cost of the process, while the quality of the white is deteriorated, owing to its deficiency in hydroxide. Too high a temperature

must be avoided, for although a high temperature increases the rapidity with which the subsalts are formed, yet it is liable to cause them to lose their water of hydration and to pass into the monoxide subsalts; the presence of these in the white lead makes it of bad colour and hence deteriorates the quality. Too little air, acetic acid, and aqueous vapour also tends to prevent the proper formation of the subsalts and, consequently, of the white lead of the best quality; too much acetic acid converts the subsalts into the normal salts and, as is well known, these do not produce white lead of good quality; besides which, being soluble in water, they are washed off the surface of the lead by the aqueous vapour which condenses on the lead, and are thus lost for the purpose of making white lead. These are a few of the principal conditions which Prof. Gardner points out as being necessary for the proper production of white lead of good quality, and, although given in connection with his own process, yet there is no doubt but that they are applicable to all chamber-processes and also to some other methods of making white lead.

The electric process is carried out in a chamber made of any convenient form and material; it is necessary, however, that it should be so constructed that the progress of the operation is readily visible. In this chamber are arranged a number of shelves covered with tin, a metal which is electro-negative to lead. Carbon, or any metal which is electro-negative to lead, may be used, but the inventor prefers tin. These shelves are connected together in succession by means of strips of tin, so that when lead is placed on them they form an electric couple. Instead of having the shelves a fixture in the chamber, they may be constructed on an open framework fitted with wheels; on this, while outside the chamber, the lead gratings are arranged, and when the shelves are full the frame and its contents are run into the chamber, but before doing so the lead is soaked in a solution of acetate or nitrate of lead. The temperature of the chamber is maintained at 120° F. by means of steam which is sent into it for that purpose. At the same time currents of acetic or nitric acid vapours, made by boiling dilute solutions of those acids, are conveyed into the chamber, or dioxide of nitrogen with acetic acid may be used. The atmosphere of the chamber must be in a misty condition, and this is brought about by regulating the current of acid vapours and steam; this state of affairs is kept up for 48 hours, when a current of pure carbonic acid gas is sent in for 2 hours, then stopped, and the acid gases sent in by themselves for 4 hours, when the admission of carbonic acid is again resumed for

2 hours ; these alternation of currents of acid gases and steam for 4 hours, and acid gases and steam and carbonic acid for 2 hours, is carried-on for 14 to 15 days, when the whole of the lead will be found to be converted into white lead. During all this time the temperature must be kept at about 120° F., and the atmosphere of the chamber misty ; it is for the purpose of closely watching the progress of the process that the chamber is fitted with windows.

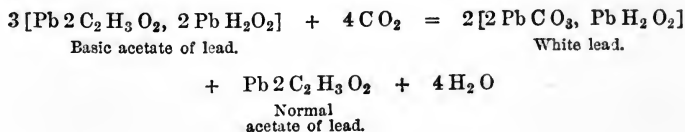
The carbonic acid gas may be prepared by any well-known method, but the inventor prefers to use a petroleum lamp as the source of it.

After the operation of making the white lead is finished, the material is not immediately removed from the chamber, but the acid gases are stopped, and steam only sent in, which serves to wash the product ; then, after a time, the current of steam is stopped, and air only admitted, when the white lead becomes dry. It is now taken out of the chamber and finished in the usual way.

The product obtained by Gardner's process is of good colour and body, and closely approaches, if, indeed, it is not equal to, Dutch white lead in its properties. One advantage said to be possessed by this process over the stack method, is that while in the latter it is essential to work with the purest lead which can be made, in the new process ordinary commercial lead gives excellent results.

3rd GROUP.—PRECIPITATION PROCESSES.

When a current of carbonic acid gas is passed through a solution of a basic salt of lead, such as the basic acetate or the basic nitrate, a white precipitate will be obtained, which is due to the combination of the carbonic acid with the excess of lead oxide contained in the basic salt ; this precipitate consists of a more or less basic carbonate of lead. At the same time, a solution of the normal salt is obtained, because carbonic acid is too weak to displace any other acid from its combination with lead. This action of the carbonic acid gas is shown in the following equation :—



although this may not accurately represent the action which goes on in the majority of cases.

Various salts of lead are used. The differences between the various processes based on the principle just described, depend upon the kind of salt used, and the method of carrying out the operation.

These processes were introduced in the early part of the century, the first patent being dated 1808, and granted to E. Noble. The process described consisted in passing a current of carbonic acid through a solution of lead acetate. A very similar method is known as Thenard's, or the French, process, and will be found described below; while another precipitation-method is known as the Kremnitz process, having been largely used there for the preparation of white lead.

The precipitation-processes based on the action of carbonic acid gas upon lead salts may be divided into two sub-groups:—
3a. Dry methods, in which the lead salt is used in the dry state, or, at the most, simply moistened. 3b. Wet methods, in which, the lead is used in the form of a solution.

3a.—DRY PRECIPITATION PROCESSES.

1. **Kremnitz Process.**—This process owes its name to having been worked at Kremnitz in Germany. It is carried on in a chamber built of brick or wood, having a number of shelves, on which is placed trays containing a paste made of litharge and either acetic acid or lead acetate, usually in the proportions of 100 lbs. of litharge to 18 pints of acetic acid, or an equivalent quantity of lead acetate solution. When the chamber is filled carbonic acid gas is sent into it, this becomes absorbed by the lead oxide present in the paste, the absorption of the gas being facilitated by raking over the paste from time to time, the mass being kept moist, as this increases the absorption of the gas. The mass originally has a yellowish-grey colour, but as the operation progresses it gradually changes into a white; and when all traces of yellow have disappeared, the operation is stopped, and the white lead which is made is first washed with water, then ground and dried.

Care is taken not to pass the carbonic acid in too long, because this would induce the formation of the normal, instead of the basic, carbonate, which means poor white lead. When carefully worked, good results can be obtained by this process.

The following analysis, presumably of a Kremnitz white lead, is given in Wagner's *Technologie*:—

Lead oxide,	83.77 per cent.
Carbonic acid,	15.06 „
Water,	1.01 „

or

Lead hydroxide,	8.21 per cent.
Lead carbonate,	91.21 „
Moisture,	0.42 „

which shows that this sample did not approach Dutch white lead in composition, but contained more carbonate.

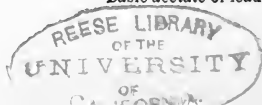
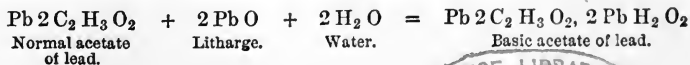
2. **Mullin Process.**—In this process, which is not now in use, litharge was ground into a paste with water; the paste was then placed in shallow lead-lined boxes, in layers of about an inch and a quarter thick, the boxes were closed by a lid, and then into them was sent currents of carbonic acid and acetic acid gases; the litharge was gradually converted into white lead. The process was, presumably, not a successful one, or it would not have gone out of use.

3b.—WET PRECIPITATION PROCESSES.

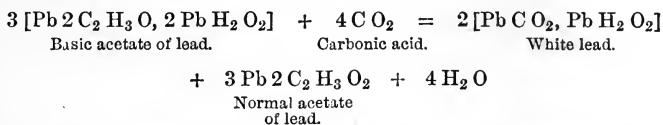
In this group of processes for the preparation of white lead, the lead is used in the form of solution, and the precipitation is effected by means of a current of carbonic acid gas. There are a large number of these processes, and many are still in use on the large scale. The differences between the various processes belonging to this group depend upon a variety of circumstances, such as the method of preparing the solution of lead, and the form of apparatus used, on which to a large extent depends the subsidiary, but not unimportant point, the method of applying the carbonic acid to the lead solution.

1. **Thenard Process.**—This process, from having been worked on a large scale at Clichy, in France, is known as the French process; it is also described in the patent granted to E. Noble in 1808.

The principle of the Thenard process, which is also applicable to many others of this group, is that when a solution of normal lead acetate is boiled with litharge, some of the latter is dissolved, and a solution of basic lead acetate, known as "Goulard's Extract," "Extract of Saturn," &c., is obtained. The reaction is expressed in the following equation:—



If a current of carbonic acid is passed through this solution of basic acetate of lead, the lead hydroxide it contains is precipitated as a more or less basic carbonate, thus —



The normal acetate which is thus re-formed can be used again for preparing a fresh solution of basic acetate of lead; of course, while, theoretically, a very little normal acetate is sufficient for the preparation of a large quantity of white lead, and there should be no loss, practically, a small quantity of new acetate has to be added from time to time to make up for the little loss which does occur.

The apparatus used in carrying out the French process at Clichy is shown in Fig. 6. In a vessel, A, of convenient size, litharge is dissolved in a solution of lead acetate, the solution being accelerated by heating the solution by means of the steam pipe, B; from this vessel the liquor in A runs into another vessel, C, in which all insoluble matter settles out. The clear solution is now run into a trough-shaped vessel, D, into which dip a number of pipes connected with the large main pipe, E, through which a stream of carbonic acid gas from the generating system, F G, flows. This system consists of an oven, F, in which is burnt a mixture of chalk and coke, from which a large quantity of carbonic acid gas is evolved; this gas is washed in the apparatus, G, by passing it through water, after which it passes into the solution of lead in the vessel, E, precipitating white lead from it in so doing; the length of time of treating depends upon the quantity and basicity of the lead solution, but usually it takes from 12 to 14 hours. At the end of this time the current of gas is stopped and the white lead allowed to settle; the clear liquor, which is a solution of the neutral acetate, is run into a vessel, H, from which it is pumped up by the pump, I, into the vessel, A, to dissolve more litharge for a fresh operation. The mass of white lead which settles at the bottom of the vessel, E, is run into another vessel, K, from whence it passes on to filters to be washed, and then it is finished in the usual way.

The product given by this process is fairly good, but liable to vary in composition from time to time, according to the strength of the solution of basic lead acetate, and to the basicity or pro-

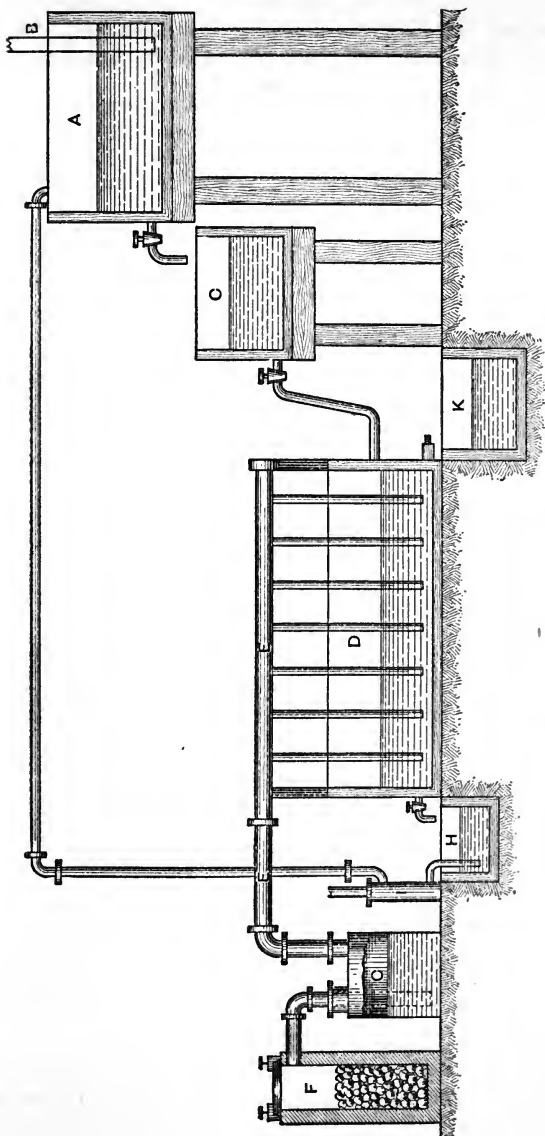


Fig. 6.—French process for making white lead.

portion of lead oxide the lead acetate has dissolved. These are points to which reference will be made in describing other processes.

2. **Cory Process.**—The same materials are used in this process as in the last, viz., basic lead acetate and carbonic acid gas, but it differs in the form of apparatus used. The process has been worked on a large scale for a long period. It was first

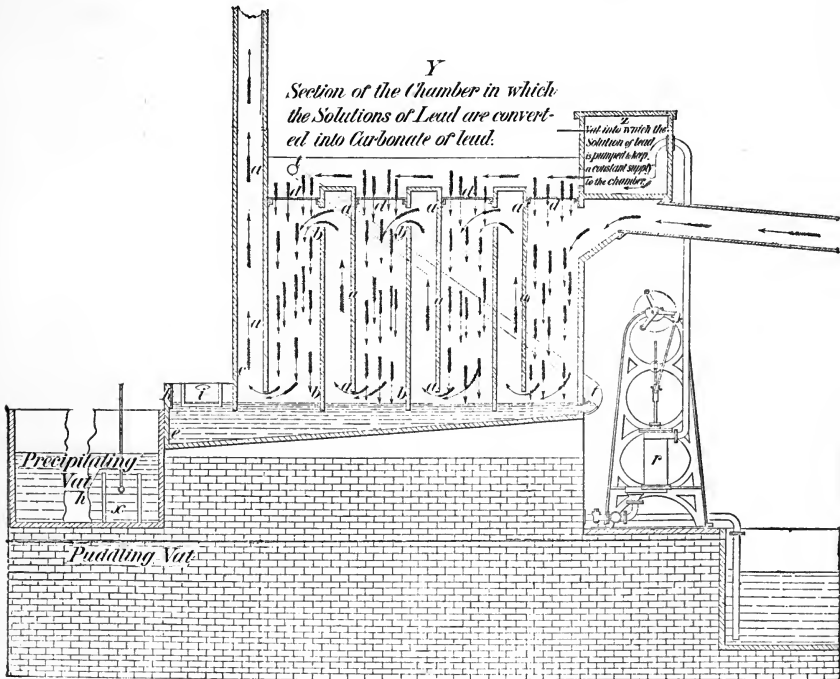


Fig. 7.—Cory's process for making white lead.

patented in 1838, and the white lead produced by it is favourably spoken of by users. The author believes that the process is still in use.

The plant used is shown in Fig. 7. A chamber is built of brickwork; the bottom is made watertight and sloping towards one end so that any liquor which may fall upon it drains away into a tank; this chamber is divided by a number of vertical

partitions into compartments ; the partitions are so constructed that each alternate one does not quite reach the top while the others do not quite reach the bottom, as shown in the figure ; the object of this is to make the carbonic acid gas, which is sent into the chamber at one end, take a circuitous course before it passes out at the other end. Above the chamber is a tank, the bottom of which forms the roof of the chamber, which bottom is perforated with a large number of fine holes, so that any liquor which may be run into the tank flows through into the chamber below, in a fine stream like rain. In another tank a solution of basic acetate of lead is prepared in the usual way, this flows into the chamber tank and from thence into the chamber ; here it comes into contact with carbonic acid gas which is sent into the chamber, the action between the lead solution and the gas being facilitated by the liquor being in such a finely divided form.

The lead solution falls down to the bottom of the chamber, and thence into settling tanks, where the white lead which is formed settles ; it is collected, washed, dried, and finished in the usual way, while the solution of neutral acetate of lead, which is also obtained, is used over again.

3. Milner Process.—Milner does not use the basic acetate of lead in his process, but prepares his lead solution by taking 4 lbs. of finely-ground litharge, and mixing it with 1 lb. of salt dissolved in 16 lbs. of water, the mixture being made in wooden tanks. The patentee states that these should be made of yellow pine ; oak-wood tanks will not do. In the tanks the mixture is well agitated for about $4\frac{1}{2}$ hours, at the end of which time it will have been converted into the basic chloride of lead. When the basic chloride has been fully formed, it is run into covered wooden tanks fitted with agitators ; through these tanks a current of carbonic acid gas passes, which, acting on the basic chloride, converts the latter into white lead. Instead of this procedure, the basic chloride may be mixed in lead-lined tanks with caustic soda, and gas is passed into the tanks, as before, until the liquor ceases to be alkaline. This point is ascertained by the workmen taking a little of the mixture out of the tanks from time to time ; if it appear viscid, forming a homogeneous mass and an even layer on the sides of the glass, then sufficient gas has not been passed in ; if, however, it forms a sort of arborescent pattern on the sides of the glass, the operation is finished ; the current of gas is then stopped, and the white lead sent to be finished in the usual way.

The process is said to yield a white lead of good colour and body, and very heavy, weighing about 200 lbs. to a cubic foot.

It was worked by the Sankey White Lead Co., but has been discontinued for some time.

4. **Martin Process.**—Martin's process for the preparation of white lead is based on the action of carbonic acid on solutions of basic acetate of lead; whether this process was ever used on the large scale the author has no knowledge. One great fault of all precipitation-processes for the manufacture of white lead is that they are apt to give a product which is more or less crystalline, a condition fatal to its being of good quality; the colour may be good, but the body is always deficient. The patentee states that this depends upon the proportion of acid solvent of the litharge to the water which is used in the process; if the water be in excess, then too much basic salt is formed, and the carbonic acid, acting too energetically upon this, causes the formation of a crystalline product; therefore the acid solvent must be in excess. Martin prepares a solution of the neutral acetate of lead in one and a-half times its weight of water, or litharge may be dissolved in acetic acid in such a way as to produce a similar solution. 3,600 gallons of this solution are placed in a tank fitted with an agitator; there is then added 4 to 6 tons of granulated lead, and half a ton of litharge. After thoroughly mixing the materials together, carbonic acid gas is passed in for an hour, when all the litharge will have been converted into white lead, then half a ton more litharge is added, and more carbonic acid; in about an hour this second lot of litharge will be converted into white lead, then more litharge is added, carbonic acid being meanwhile sent in; these additions of litharge are continued hourly until sufficient white lead has been formed, when it is collected and finished in the usual way. If thought desirable, instead of adding the litharge in lots every hour it may be run in in a constant stream. During the operation the temperature is maintained at about 100° F.

The distinctive feature of this process is using the litharge in an undissolved form, and strong solutions of lead acetate. In the absence of practical experience of the process it is not easy to speak definitely on the effect of using such strong solutions; but, judging from the known effects of using strong solutions on the character of precipitates obtained in other cases, one would naturally imagine that the white lead formed would have a crystalline character, and not that amorphous condition which is required in good white lead, still the patentee states that such is not the case.

When the principles which underlie these precipitation-processes are considered, it becomes evident that the character

of the white lead, both chemically and physically, materially affects its value as a pigment. This character will depend upon the character of the solution of lead which is used, the temperature at which the reaction between the carbonic acid gas and the lead salt takes place, and the strength of the solutions used; on these points information is scanty, and very few of the inventors of white-lead processes have mentioned the influence of any of them. The character and basicity of the lead salt will have some influence on the result; the basicity should be due to the presence of lead hydroxide, and not to lead oxide, or, at all events, the latter should be present in only small quantities. To ensure the production of lead hydroxide, water seems to be necessary, and therefore should be used in sufficient quantity. The quantity of carbonic acid should be so regulated that not more than two-thirds of the base present is converted into carbonate; if too much gas is used, then all the base will be liable to be converted into carbonate, and the white lead has a tendency to become crystalline; the difficulty is to ascertain when sufficient gas has been used. The strength of the solution of lead will also have some influence, but the diversity of opinion among white-lead makers as to the proper strength is great; some prefer strong solutions, others weak ones. As a rule, weak solutions give the finest precipitates, and strong solutions give the coarsest. The temperature at which the operation is conducted will have some little influence; cold solutions will cause the formation of fine precipitates, while hot solutions tend to give rise to crystalline precipitates, due to the fact that the reaction between the carbonic acid and the lead salt takes place too readily; still it is not desirable to work with solutions that are too cold; the best temperature is from 100° to 120° F.

5. **Fourmentin Process.**—This was proposed many years ago, and somewhat resembles Milner's process. Litharge is taken and treated with salt in such proportions as to convert it into oxychloride of lead; this body is placed along with water in a number of cylindrical vessels fitted with radial beaters. Carbonic acid is sent in, while the temperature is maintained at the boiling point. When the reaction between the acid and the lead has finished, the current of gas is stopped and the product run into a boiler, in which it is boiled with a quantity of finely-powdered carbonate of lime, equivalent to the amount of salt used in the preparation of the oxychloride, this boiling being continued until, on taking out a sample, and filtering off and testing the clear liquor with ammonia and

ammonium sulphide, no precipitate forms; the period of boiling varies from two to four hours. When the boiling with the carbonate of lime has been continued long enough, the operation is stopped, and the white lead allowed to settle out, collected and finished in the usual way.

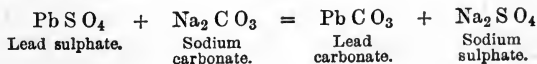
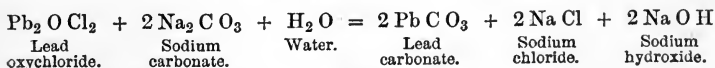
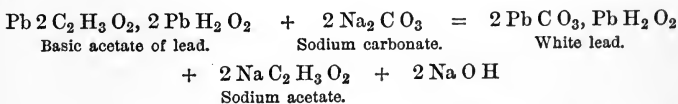
6. Spence Process.—The principle of this process consists in boiling a salt of lead (the oxide or carbonate gives the best results, but the sulphate or other salt which can be dissolved by caustic soda may be used) with a solution of caustic soda until the alkali is saturated with lead; then a current of carbonic acid is passed through the liquor, and white lead is precipitated, while carbonate of soda is formed. The latter can be causticised by means of lime, and used over again. The white lead which is precipitated is collected, washed, and finished in the ordinary way. This process has not been used on a commercial scale.

7. MacIvor Process.—The principle of this process depends upon the fact that when litharge is acted upon by acetate of ammonia under the combined influence of heat and pressure, it is converted into basic acetate of ammonia and lead, while ammonia is liberated in the free condition, and dissolves in the water which is present to form the liquor ammonia of commerce. Then, when a current of carbonic acid gas is passed through the mixture of basic acetate of lead and ammonia, the lead is precipitated as basic carbonate or white lead, of good colour and covering power; while acetate of ammonia is re-formed and can be used again for dissolving a fresh batch of litharge. The process is carried out somewhat in the following manner:—Into a digester made of strong iron plate lined with lead, is placed a solution of acetate of ammonia of not less than 5 per cent. strength and a quantity of litharge which has been previously very finely ground. The proportions of the two will depend upon the strength of the solution of ammonia acetate which is used; for that given, 1 ton of litharge is used for 1,200 gallons of liquor. The digester is closed. The acetate solution is sent through a heater so that it may have a temperature of from 60° to 100° C., and then into the digester, passing into it from a pipe fitted with a conical spreader at its lower end; the acetate solution flows upwards through the litharge, effectually agitating the mass and so assisting its solution; from the digester the liquor is drawn off from the upper portion by means of a pump and passed through the heater and again into the digester, this cycle of flow being continued until all, or nearly all, the litharge is dissolved. The solution of basic acetate of lead and ammonia is now passed

through a filter-press into a cooler, from which it flows into a carbonator. The cooling of the liquor causes the separation of much of the basic acetate of lead in the form of fine crystals, so that in the carbonator a fine magma is presented to the action of the carbonic acid gas, which is sent into it from any convenient source. A circulation of the mass in the carbonator is kept up by drawing off from the upper portion of the carbonator and forcing it by means of a pump through a pipe, with a conical spreader at its end, to the bottom of the carbonator; in this way every part of the mass of liquor and crystals is made to come in contact with carbonic acid gas. The white lead is rapidly formed as a fine white precipitate. When it is considered that the carbonation is finished the whole mass is passed through a filter-press, so as to separate the white lead formed, while the liquor, which consists of a solution of acetate of ammonia, together with unchanged basic acetate of lead and free ammonia, is sent to the digester to be used again. The process is a rapid one; the solution of the litharge in the acetate of ammonia does not take long, while the conversion of the basic acetate of lead into white lead in the carbonator is almost instantaneous. The process is being worked by a limited company.

4th GROUP. PRECIPITATION PROCESSES WITH ALKALINE CARBONATES.

When a solution of sodium carbonate, or other alkaline carbonate, is added to a solution of lead, a white precipitate of a more or less basic carbonate of lead is obtained; insoluble basic or neutral salts of lead, such as the oxychloride or the sulphate, are also acted upon by alkaline carbonates, and basic lead carbonate is formed; these reactions are formulated in the following equations:—



The chief difficulties met with in carrying out the processes

depending upon the action illustrated in the above equations, are to prevent the formation of a highly crystalline neutral carbonate and to ensure that the precipitate shall have the necessary amount of basicity ; for, as will be seen from the above equations, the tendency is to form the normal carbonate of lead instead of the basic carbonate.

These methods of preparing white lead early attracted attention from white-lead makers, and many and various have been the processes which have been patented and tried for the manufacture of the pigment by such methods. While there is no doubt that good white lead can be made by them, yet the results seem to be so variable that from a commercial point of view these processes have always been failures.

The first patented process belonging to this group dates from 1797 when the Earl of Dundonald secured a patent for making white lead from the oxychloride of lead.

1. **Dundonald Process.**—Litharge is taken and is treated with sufficient salt and water as to convert it into the oxychloride of lead, in the manner which will be found more fully detailed on p. 29. The insoluble oxychloride is collected, washed to free it from alkaline salts, then boiled in a solution of potash (potassium carbonate), when it is converted into white lead, which is collected, and, after washing, dried ; it is then ready for use. A very similar process was patented some years later by James Kier. No record exists as to whether this process was much, if at all, used on the large scale.

2. **Pattinson Process.**—Mr. Hugh Lee Pattinson, a large lead-smelter of Newcastle, has prepared white lead by many processes ; "Pattinson's white lead" (which see) is the oxychloride of lead. The process, which comes under the present group, has for its object the preparation of ordinary white lead. Chloride of lead prepared by any convenient process is mixed with carbonate of lime in the proportion of their chemical equivalents, 278 to 100, and the mixture is ground with water for several hours, then allowed to stand all night, the clear liquor (which consists principally of a solution of chloride of calcium) run off, more water added, and the grinding resumed for a few hours ; then it is again allowed to stand all night and the clear liquid again drawn off. These operations are continued until the effluent water is tasteless. The white lead, after being finished in the usual manner, is ready for use. Instead of the process just described a solution of the carbonate of lime or of carbonate of magnesia, made by means of carbonic acid, is used to act on the lead chloride.

In another modification of the process, chloride of lead and carbonate of calcium are placed in a revolving cylinder and a current of carbonic acid gas sent into the mixture, preferably the gas is used at a pressure of four or five atmospheres; after four days the aqueous liquor, which is, as before, a solution of calcium chloride, is drawn off, more water run in and the gas again passed in for two days longer, when the reaction is completed, and the white lead only requires finishing to be ready for use. This process does not seem to have been much used.

3. **Dale and Milner Process.**—The inventors take litharge or a basic salt of lead and grind it with water and bicarbonate of soda for some time, when white lead is formed. This process was worked on a large scale for a short time, but it was superseded by Milner's process described above. A process patented by *Isham Baggs* was almost identical with this. The results were not very satisfactory as the white lead obtained was rather too crystalline in structure.

4. **Watt and Tebbutt Process.**—This consisted in treating sulphate of lead, first with lime, then with potash. Cooper uses 25 lbs. of sulphate of lead to 10 lbs. of potash. The action of alkaline carbonates upon lead sulphate is, at the best, but imperfect, and a complete change into carbonate is never obtained.

5. **Delafield Process.**—Delafield uses nitrate of lead, which he prepares by dissolving one cwt. of litharge in one cwt. of nitric acid and just enough water to form a saturated solution. This is heated by steam to a temperature of about 200° F. When a hot solution of 70 lbs. of potash is run in, white lead is precipitated, which is collected and, after washing, dried. The product is liable to contain too much carbonate and, therefore, to be deficient in body.

6. **Rowan Process.**—This resembles the Watt and Tebbutt process, only the action between the lead salts and the alkaline carbonate is effected under a pressure of from 30 to 40 lbs.

7. **Lowe Process.**—In Patent No. 9,122 of 1887, a process for making white lead is described, which consists of the following operations:—50 lbs. of lead acetate, or 43·6 lbs. of lead nitrate, are dissolved in 25 to 30 gallons of water; to this solution is then added 23 lbs. of solid bicarbonate of soda or 26·4 lbs. of solid bicarbonate of potash, when a precipitate of a more or less basic carbonate of lead will be obtained. In another vessel 25 lbs. of lead acetate and 15 lbs. of litharge are digested with 12½ gallons of water for 8 to 10 hours, when the product which is obtained is mixed with the precipitate obtained in the first

instance. White lead is formed and is collected and finished in the common way. An analysis of a sample of white lead made by this process is given in the patent, as follows:—

Lead monoxide, Pb O,	86·185 per cent.
Carbonic acid, C O ₂ ,	11·270 „
Water, H ₂ O,	2·545 „

which differs but little from that of the Dutch process white lead.

8. Condy Process.—This process was patented in 1881, and has been worked on a large scale; but whether the process is now in use or not the author is unaware. In this process, acetic acid of 1·045 specific gravity is diluted with about five times its volume of water, and allowed to act on granulated lead until a solution of lead acetate of 1·2 specific gravity is obtained; this solution is evaporated to dryness, when the bibasic lead acetate is obtained. 275 lbs. of bibasic acetate of lead, 112 lbs. of litharge and 5 gallons of water are ground together into a paste. Instead of preparing the bibasic acetate the neutral acetate may be used; in this case, 189 lbs. are ground with 229 lbs. of litharge and 21 lbs. of water for a few hours, and then left for 48 hours. In either case there is formed the tribasic acetate of lead. The mass is dissolved in 10 times its weight of water, and, then, for every 112 lbs. of litharge in the mass 84 lbs. of solid bicarbonate of soda is added; this precipitates the white lead, which is finished in the usual way. A modified process was described in a later patent. One part of acetic acid of specific gravity 1·045 is mixed with $12\frac{1}{2}$ times its weight of water, and the dilute acid so obtained allowed to act upon granulated lead until a solution of specific gravity 1·040 is obtained; this is mixed with water, and, then, for every 60 lbs. of acid used in preparing the solution, 30 lbs. of solid bicarbonate of soda are added, and the white lead is precipitated.

The white lead prepared by this process has been favourably spoken of; it has a good colour and covering power. In chemical composition it resembles white lead, but the process appears to be somewhat variable in its results, and, therefore, not commercially practicable.

5th GROUP. MISCELLANEOUS PROCESSES.

Besides the processes described above, others have been proposed or patented from time to time which are perhaps just worth mentioning, as showing what has been done by

inventors towards the preparation of white lead by other means than the old Dutch process. Some of these processes do not come within the groups of processes described above, others fall into one or other of them; but as they are only of small importance, and as, in some cases, it is doubtful whether they were ever worked on a large scale, they have been relegated to this division of white-lead processes for description. The processes are rather numerous, and will only be given in outline; for further details the reader is referred to the records of the Patent Office.

Torassa proposed a curious process, which is of interest on account of its novelty only, not from any practical value it may possess. Lead is granulated, and then placed, with a small quantity of water, in a revolving box, or a box fitted with agitators; in this it is worked until it forms a very fine mud, which is again agitated with air until it has been converted into white lead. The process must have been a slow one, as the amount of carbonic acid in the air is small, and can only convert in a given time but a small quantity of fine lead into carbonate. *Wood*, a more recent inventor than *Torassa*, proposed to use the same process, but to hasten the preparation of the white lead by agitating the fine lead mud with carbonic acid; but even this was not sufficient to make the process a practical success.

Mullins proposed to make white lead by an ingenious but, from a practical point of view, unsuccessful method. Sponges, saturated with a solution of basic acetate of lead, were suspended by porous strings in a chamber into which carbonic acid was passed; this, of course, transformed the basic acetate into basic carbonate of lead. The sponges were kept saturated with a solution of acetate by connecting the porous strings with a tank containing the solution, which, by capillary attraction, passed along the strings to the sponges. The process was not used on a large scale.

Martin prepares carbonate of lead so that it shall contain a slight excess of carbonic acid. Hydroxide of lead is prepared by thoroughly agitating granulated lead with air and water. The two bodies are mixed together in the proportion of 8 lbs. of hydroxide to one ton of carbonate, the mixture being made by grinding with water into a paste.

Lewis prepares what he calls white lead from lead or lead ores, by mixing these with anthracite coal, and heating the mixture in a Wetherill zinc furnace with a powerful blast of air; the white lead sublimes, and is collected (see p. 18).

Although the product is spoken of as white lead, it is probably the sulphate of lead.

Button and Dyar treat the basic nitrate of lead with carbonic acid gas.

Button and Young take the lead nitrate, and pass a current of carbonic acid until the liquor becomes saturated with the gas, when caustic soda is added in slight excess; white lead is precipitated; it is allowed to settle, and, after pouring off the supernatant liquor, is digested with lime water, and then washed and dried.

Maxwell-Lyte proposes to use spongy lead in the ordinary chamber process, with the view of facilitating the action of the gases on the lead, and so making the process more rapid.

Woolrich used a process not unlike that of Torassa; he provides a revolving box, into which he places granulated lead; by the attrition, which occurs during the revolution of the box, the lead is gradually converted into a fine powder; a solution of basic acetate of lead is also placed in the box, and this, to some extent, by chemical action facilitates the operation. Every twelve hours the action is stopped, and the lead mud formed is washed out by means of a current of basic lead acetate liquor, through which is afterwards passed carbonic acid gas to transform the lead into white lead.

Ozouf uses a solution of the tribasic acetate of lead, places this in a closed vessel fitted with agitators, and then sends in a current of carbonic acid gas to precipitate the white lead.

Cookson has a process not unlike that of Cory; he constructs large chambers, into which he throws a solution of basic acetate of lead in the form of a spray; the spraying being done by means of a jet of carbonic acid gas.

Other methods have been proposed, but they are all modifications of those which have already been described.

COMPOSITION AND PROPERTIES OF WHITE LEAD.

White lead is sold commercially in two forms. One is a heavy white powder, having a specific gravity of about 6.47, and weighing about 180 lbs. to the cubic foot; it is stated that some processes yield white lead weighing as much as 200 lbs. to the cubic foot. The other form is that of a paste containing about 8 per cent. of linseed oil.

The chemical composition of white lead has already (p. 17) been pointed out. It is a basic carbonate of lead formed by the union of two molecules of lead carbonate, $PbCO_3$, with one

molecule of lead hydroxide, PbH_2O_2 ; this is the composition of the best make of Dutch white lead, which has all the good properties of white lead in the highest degree of perfection.

It is scarcely necessary to point out that as white lead is made by many processes it must necessarily vary in composition; indeed the white leads yielded by the same process do not always have the same composition, as is evinced by the analyses given here and on p. 19; these have been collected from a variety of sources.

ANALYSES OF WHITE LEADS.

	1.	2.	3.	4.	5.	6.	7.
Lead monoxide, PbO ,	86.35	85.93	83.77	85.93	84.42	86.5	86.24
Carbonic acid, CO_2 ,	10.44	11.89	15.06	11.89	14.45	11.3	11.68
Water, H_2O ,	2.95	2.01	1.01	2.01	1.36	2.2	1.61
	99.74	99.83	99.84	99.83	100.23	100.0	99.53

from which the composition of the white leads can be calculated to be—

Lead carbonate, $PbCO_3$,	63.35	72.15	91.21	71.93	87.42	68.36	70.87
Lead hydroxide, PbH_2O_2 ,	36.14	27.68	8.21	27.88	12.33	31.64	28.66
Moisture,	0.25	...	0.42	0.02	0.48

No. 1. English make. Made by the Dutch process; of very good quality.

No. 2. English make. Made by the Dutch process; of good quality.

No. 3. Krems white. Made by precipitation with carbonic acid gas; this sample is deficient in body although of good colour.

No. 4. German make. Precipitated by sodium carbonate; it is only of medium quality.

No. 5. German make. Precipitated by carbonic acid gas; of good colour, but deficient in body.

No. 6. German make. Made by the Dutch process; a good white.

No. 7. German make. Made by precipitation with carbonic acid gas; quality fair.

The second form in which lead is sold is that of a paste with linseed oil. To make this, the dry white lead, above described, is first mixed in a mixing mill, with about 8 to 9 per cent. of its weight of raw linseed oil; then it is run through a grinding mill several times, to ensure a thorough mixture of the oil and white lead. This form is much favoured by painters, as it is more readily miscible with oil and turps to make into paint.

The following are two analyses of ground white lead:—

Lead hydroxide, PbH_2O_2 ,	65.96	71.14	per cent.
Lead carbonate, $PbCO_3$,	25.19	20.45	„
Insoluble,	0.70	...	„
Oil,	8.34	8.34	„

In making this ground white lead only the best raw linseed oil should be used; boiled oil is not admissible, as there would be too much tendency for the lead to become a hard dry mass before it could be used. It is customary to keep ground white lead under water to prevent it drying up too rapidly. Besides its use by painters, this form of white lead is also largely used for other purposes, as a cement for gas-piping, &c.

White lead is soluble in dilute nitric acid, and in acetic acid with effervescence, due to the evolution of carbonic acid gas. It is also soluble in boiling dilute hydrochloric acid with effervescence; on cooling the solution fine transparent needle-shaped crystals of lead chloride separate out. Boiling with sulphuric acid decomposes the white lead, insoluble lead sulphate being formed.

Solutions of white lead in acids give white precipitates of lead sulphate with sulphuric acid; of lead chloride with hydrochloric acid, soluble on boiling in water; and of lead carbonate with sodium carbonate.

Neutral solutions of white lead give a yellow precipitate of lead chromate with potassium bichromate, and a black precipitate of lead sulphide with sulphuretted hydrogen and solutions of sulphides.

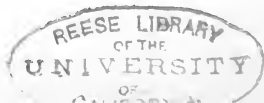
As a pigment white lead possesses all the good qualities desired by a painter—viz., good colour, body or covering power, and permanency. It is distinguished from all other pigments by the ease with which it mixes with oil and by forming a paint which readily flows from the brush, whereas most pigments, as for instance, barytes, tend to work what the painter calls slimy or livery, and streaky; white lead does not exhibit this property, but flows freely and evenly from the brush. This feature is due to the lead hydroxide in the white lead combining with some of the oil and forming a lead soap which, dissolving in the rest of the oil used in the preparation of the paint, forms a kind of varnish; this varnish takes up the lead carbonate to which is due the body or covering power of the pigment. Sometimes this chemical combination between the lead hydroxide and the oil extends to the lead carbonate and then the white lead loses its opacity and becomes more or less transparent or horny; the conditions most favourable to the production of this change, which is of rare occurrence, are not properly known. This fact of the white lead forming a chemical combination with the oil is well known to colour makers, who have endeavoured, by the addition of basic bodies, to bring about a similar action in the case of other white pigments, such as zinc white and barytes, but so far without any great success.

When exposed to light and air white lead is fairly permanent and will resist exposure to normal conditions for a great length of time; on the other hand, when exposed to the fumes of sulphuretted hydrogen and other sulphureous gases, white lead turns brown or black through the formation of the black sulphide or lead. The production of this body is more likely to occur in large towns, such as London and Manchester, where large quantities of gas are used for lighting and other purposes, which usually contains some sulphuretted hydrogen or other sulphur compounds. By oxidation this black sulphide can be transformed into the white sulphate of lead; the only agent which can be safely used for this purpose in restoring paintings which have become discoloured is peroxide of hydrogen, but the action of this body is very slow and is much interfered with by the oil which is present.

White lead can be mixed with all pigments except those which, like cadmium yellow, ultramarine or king's yellow, contain sulphur; such pigments sooner or later cause the formation of the black sulphide and thus bring about the discolouration of the pigment or paint.

White lead is frequently adulterated, the pigment most used for this purpose being barytes, because it more nearly approaches white lead in specific gravity, and is, on that account, not so readily detected; whereas the use of whiting or gypsum would soon be detected on account of the great difference in weight between genuine white lead and white lead adulterated with them.

This adulteration of white lead is exceedingly common and is well understood by makers and dealers; in fact it is the custom for makers to send out several qualities of commercial white lead distinguished as "genuine," "No. 1," "No. 2," and so on; the degree of adulteration being regulated by the price which is paid for the product. The question whether this is adulteration is a matter of opinion; if by adulteration one means the admixture of cheap products with dear products with a view of deceiving purchasers of the latter, then the admixture of barytes with white lead under the conditions named is not adulteration, for the purchaser knows what he is buying, and only pays a fair price for such mixed white leads. The author is, however, of opinion that this custom of mixing barytes with white lead would be much better honoured by the breach than the observance of it.



ASSAY AND ANALYSIS OF WHITE LEAD.

White lead may be assayed for colour and covering power by the usual methods (see Chapter X.).

Dry White Lead.—The purity of this pigment is ascertained by dissolving some of the lead in pure dilute nitric acid (1 acid, 2 water); strong nitric acid does not dissolve white lead owing to the insolubility of the lead nitrate which is formed in the acid; the ordinary commercial nitric acid contains sulphuric acid, which would lead to the formation of the insoluble sulphate of lead, the production of which might lead to the condemnation of a pure sample.

On adding dilute sulphuric acid to the solution, after diluting it with water and filtering off the precipitate of lead sulphate thus obtained, no further precipitate should be obtained on successively adding ammonia, ammonium sulphide, and ammonium oxalate to the filtrate.

A white precipitate with ammonium sulphide would indicate the presence of zinc white, which is a rare thing to find with white lead; a white precipitate with ammonium oxalate would indicate the presence of whiting.

The insoluble residue, if any, will consist most probably of barytes, as other adulterants (for reasons already pointed out) are rarely used; still any lead sulphate, china clay, gypsum, or strontium sulphate which may be used would also be left as an insoluble residue on treating white lead with dilute nitric acid. To distinguish these bodies, boil the residue in hydrochloric acid and place the solution on one side to cool; if crystals of lead chloride separate out and the solution gives a white precipitate with barium chloride, then lead sulphate is present.

The hydrochloric acid solution should be diluted with water and sulphuretted hydrogen passed through it; the black precipitate of lead sulphide which may be obtained can be disregarded; this is filtered off and the filtrate boiled for some time to concentrate it and to drive off the sulphuretted hydrogen it contains. Then ammonia is added, when a white precipitate of alumina may be obtained indicating the presence of china clay; this is filtered off, and to the filtrate is added ammonium carbonate, which will precipitate any calcium that may have been added, in the form of gypsum or whiting.

A little of the insoluble residue from the hydrochloric acid should be held on a piece of platinum wire in the lower part of a Bunsen flame when, if it contains barytes, the flame will be

coloured green ; if strontium sulphate is present a crimson flame will be obtained. This test is not always easy to carry out, but with a little care the coloured flames can be obtained, and they are good proof of the presence of the pigments named.

A quantitative analysis of white lead may be made as follows :—

Weigh out 2 grammes and dissolve them in a beaker with the smallest possible quantity of pure dilute nitric acid, remove the insoluble matter by filtering, wash the residue well with warm water, adding the first wash waters to the filtrate, then dry the residue, place the filter paper and its contents in a weighed crucible and burn the paper ; when completely burnt allow the crucible to cool in a desiccator and then weigh it. From the weight so obtained deduct the weight of the crucible and of the filter-paper ash, the difference is the weight of the insoluble residue.

To the filtrate add dilute sulphuric acid and a little alcohol, filter off the precipitate of lead sulphate which is obtained, wash it dry and burn it in a crucible as before. By multiplying the weight of the lead sulphate so obtained by 0.73554 the weight of *lead oxide* in the white lead can be found.

The *carbonic acid* can be ascertained by treating 2 grammes of the white lead with nitric acid in a Schrotter's or other form of apparatus for the estimation of carbonic acid.

The *water* may be determined by taking the difference between the amounts of lead oxide and carbonic acid thus found and 100.

Hygroscopic water can be ascertained by heating 2 grammes in an oven at 110° to 120° C. until no further loss of weight occurs.

If the white lead be adulterated with *barytes*, *lead sulphate*, *china clay* or some of the other insoluble white pigments, these will be left behind as an insoluble residue on treatment with nitric acid ; their amount is ascertained by filtering off, washing, drying, and burning the residue in a weighed crucible in the usual way. Soluble adulterants like *whiting*, *strontium carbonate*, *barium carbonate*, and *magnesite* will be dissolved ; if the presence of these is suspected, to the filtrate should be added more dilute sulphuric acid, which will precipitate the lead and barium ; this precipitate can be filtered off, the two can be separated by boiling with hydrochloric acid, which dissolves the lead sulphate but not the barium sulphate. To the filtrate ammonia and ammonium oxalate are added ; this precipitates the calcium and the strontium, while the magnesite (if present) will remain in solution, and can be precipitated by sodium phosphate. It is not necessary to describe in detail the methods of separating these

adulterants any further ; some notes bearing on this point will be found in the descriptions of each individual pigment, while reference should be made to works on quantitative chemical analysis, such as that of Prof. Sexton, for fuller details.

By multiplying the weight of the carbonic acid by 5.05 the amount of lead oxide with which it is combined can be calculated ; the two amounts added together give the quantity of lead carbonate in the white lead. Deducting the amount of lead oxide combined with the carbonic oxide from the total present, and multiplying this difference by 0.077, gives the amount of water combined with it to form lead hydroxide, and the two amounts added together gives the amount of the latter body present.

Paste White Lead can be quantitatively examined as follows :—Two grammes are treated with strong nitric acid at a gentle heat ; this converts all the oil into an insoluble greasy matter, of which no account need be taken ; the process then becomes identical with that for dry white lead. Should it be desired to ascertain the amount of the oil, then 10 grammes must be weighed into a filter paper and placed in a Soxhlet or other form of fat-extractor and the oil extracted by means of petroleum ether ; the ethereal solution is then run into a weighed glass, the ether evaporated off and the oil weighed. If a fat-extractor is not available it will suffice to agitate the white lead with some petroleum ether in a beaker, allowing the pigment to settle, pouring off the liquid into a weighed glass, again pouring on more ether, and again allowing the white lead to settle ; the ether is poured off into the glass, or the mass may be filtered. Finally, the ether is evaporated off as before.

It is sometimes recommended to burn off the oil from the white lead in a crucible, but this course is not so satisfactory as treating it with petroleum ether, as not only is the oil burnt off, but the white lead is decomposed ; whereas in the ether method the lead is left in its original form for further examination if necessary.

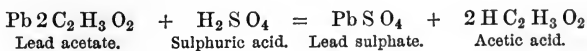
SULPHATE OF LEAD PIGMENTS.

Sulphate of lead, $PbSO_4$, forms the basis of a number of white pigments which are made on a large scale and sold under a variety of names, such as Patent White Lead, Non-poisonous White Lead, Sublimed White Lead, &c. These do not consist entirely of lead sulphate but contain other bodies, such as zinc oxide, barytes, magnesia, &c., in varying quantities ; they are

made by different methods, and most of those now sold are produced by patented processes.

Lead sulphate can be made by dissolving lead in strong sulphuric acid, the action is, however, but slight and does not form a commercial method of manufacture. It is mostly made by adding sulphuric acid to solutions of either lead acetate or lead nitrate; perhaps the best method is that where lead acetate is used.

Metallic lead is granulated by melting and pouring the molten lead into cold water; the object of granulating is to obtain the metal in such a form as to expose a large surface to the action of acids and air. The granulated lead is placed in a large tub fitted with a closed steam coil so that the action of the acid may be facilitated by heat, if necessary. Acetic acid diluted with its own volume of water is poured on to the lead; the action of the acid is at first rather sluggish, but by allowing the action to go on for about 12 hours, then running off the acid and leaving the lead in the tub without any liquor, a certain amount of oxidation goes on, resulting in the formation of a deposit of oxide on the lead, so that when the acid is again admitted to the lead, the acid acts more rapidly, and a strong solution of lead acetate is soon obtained; this action is facilitated by a gentle heating of the contents of the tub. From the tub the solution is run into a large wooden vessel and to it is added strong sulphuric acid in small quantities at a time with constant stirring; lead sulphate is thereby precipitated. Care is taken that the amount of sulphuric acid used is not sufficient to throw down all the lead, but that some of the latter is left in solution. The lead sulphate is allowed to settle, and then the clear supernatant liquor is pumped back again into the lead tub, for it contains all the acetic acid; for, as will be seen from the equation—



acetic acid is reproduced as the result of the reaction which goes on between the lead acetate and the sulphuric acid, and this acetic acid can be used over again for preparing fresh solution of lead for precipitation; thus a comparatively small quantity of acetic acid may be used to prepare a large quantity of lead sulphate; theoretically speaking, beyond the first charge no more acetic acid is required, but practically, there is a small loss which requires to be restored by new additions of acid from time to time.

The sulphate of lead which is precipitated is washed with water, drained on a filter, and dried; after which it is ready for use as a pigment, or can be combined with other white pigments if desired.

The acetic acid used should be as pure as possible; the usual commercial variety of a strength of about $1.050 = 10^\circ$ to 12° Twaddell is sufficiently good for the purpose; this contains about 35 per cent. of actual acetic acid, although some makes contain more. 100 lbs. of it will dissolve about 60 lbs. of lead supposing all the acetic acid exerts its solvent power, but in practice this never or but rarely happens, nor indeed is it necessary that it should. From 20 to 28 lbs. of sulphuric acid will be required to precipitate the lead dissolved by this quantity of acetic acid. These figures are only approximate and are given simply as guides to actual practice.

Lead sulphate has the formula $PbSO_4$, and contains

Lead oxide, PbO ,	73.55	per cent.
Sulphuric anhydride, SO_3 ,	26.45	,,

and of metallic lead 68.31 per cent.

It is a white, somewhat crystalline, and very heavy powder, its specific gravity being about 6.3. It is only slightly soluble in water, insoluble in dilute acids and in alcohol, but soluble in solutions of ammoniacal salts, and in strong sulphuric acid; from the latter solution it is precipitated on the addition of water. Boiling concentrated hydrochloric acid dissolves it, and crystals of lead chloride fall down as the solution cools.

As a pigment it is not satisfactory, its crystalline character reduces its body and covering power, causing it often to work streaky or livery under the brush; this defect can be remedied to some extent by grinding it. It is not readily acted upon by sulphuretted hydrogen, and is, therefore, more permanent than white lead under exposure to air. Owing to its solubility being less it is free from the poisonous character of white lead, and, therefore, white pigments containing it are often sold as "non-poisonous white leads." Its colour or hue is a good white, but slightly yellower in tone than white lead and about equal to barytes.

It is used as a diluent in the manufacture of pale chromes.

Many have been the attempts to make lead sulphate the base of commercial white leads, the records of these are to be found in the publications of the Patent Office, where they lie buried in an almost unknown condition, and it would really be most instructive for colour-makers and would-be inventors if they

would peruse these records and see what has been done in the past. A few of these inventions may be briefly noticed here, and a fuller description given of such as are at present used on a large scale.

Richardson, in 1839, patented the use of the sulphate only as a pigment; in 1853, *Carter & Marriott* prepared a chloro-sulphate of lead made by treating 100 lbs. of litharge with 25 lbs. of salt, and the product so obtained with 5 lbs. of sulphuric acid. *Woods*, in 1866, took out a patent for the preparation of a white pigment from lead fume, which is a mixture of lead, lead oxide, and lead sulphate; this he treated with hydrochloric acid thus forming a chloro-sulphate; or he calcined the fume in a furnace, whereby it was converted into a white mixture of lead oxide and lead sulphate, which was then treated with hydrochloric acid as before. *Groves*, in 1826, treated galena with potassium nitrate and sulphuric acid, whereby the lead sulphide was converted into lead sulphate, which was dried and sold as a pigment. In 1866, *Messrs. Bell & Fell* patented the use and preparation of what they called a sub-sulphate of lead, prepared by precipitating a solution of lead nitrate with sulphuric acid and then boiling with an alkali.

SUBLIMED WHITE LEAD.

This product is the invention of *G. T. Lewis*, and was first patented in 1879. About 1870 a vein of ore containing both lead and zinc, being a mixture of galena and blende, was discovered in America; this was smelted for lead, which, owing to it being different in properties from ordinary lead, was distinguished as "Bartlett lead;" the presence of zinc in lead ores is very detrimental, as the zinc cannot wholly be removed from the lead, while it imparts to it properties which, by causing it to become hard and brittle, prevent its application to those uses for which lead is of great service. The process of white-lead making now to be described was to some extent devised to utilise this lead-zinc ore.

The manufacture of sublimed lead depends upon two facts, which also are the principles that underlie some of the ordinary processes of lead smelting—first, when lead ore (galena, lead sulphide) is heated in a furnace with access of air it undergoes oxidation, partly to lead oxide, PbO , partly to lead sulphate, $PbSO_4$, the amount of the oxidation depending upon the amount of air which comes in contact with the ore; if this is small then

the sulphate is mostly formed. The temperature also has some influence on the result; in fact, it is probably the chief factor in the process. If low, then the sulphate is chiefly formed; if high, this is likely to be decomposed into oxide and sulphur dioxide. Secondly, during the operation of lead smelting a large proportion of the lead is carried off in the form of "fume," which collects in large chambers or flues built for the purpose. This lead-fume is a mixture of metallic lead, lead oxide, lead sulphate; if there be any zinc in the ore it will be mostly found in this fume. It has frequently been noticed that the composition of the fume varies from time to time, according to the conditions under which the furnaces are being worked. Lewis proposes to utilise the two principles laid down and, by carrying out the process in such a manner that the great bulk of the fume produced consists of lead sulphate, to prepare a white pigment from any lead ore. This is effected in the Lewis and other processes based on the same principle by causing the operation to be carried out in a blast furnace.

The preparation of sublimed white lead takes place in two stages; the first may be called *the fume stage*, in which the lead ore is transformed into fume of more or less complex composition; the second stage may be called *the colouring stage*, in which the pigment is made of a proper degree of whiteness.

In the first stage a furnace is used resembling the Wetherill zinc furnace. Four of these are placed back to back and side by side, and is hence not unlike four American lead-smelting hearths. The furnace is worked from two sides, known as the fronts; a water back, containing tuyeres, is also placed between the bench of furnaces; above the water back is an air chamber divided into two compartments by a partition, so arranged that the air which enters into one of these compartments passes to one front of the bench of furnaces, while the air in the other passes to the other front. This air is heated by passing through the hot walls of the furnaces, and by suitable means is sent as a powerful blast through the tuyeres into the hearth of the furnace, and through any ore which may be on the hearth. The ore is placed on the hearth of the furnace with the fuel necessary to effect its melting, and air is sent through it; part of the lead is reduced to the metallic state, and is collected by being allowed to flow out of the furnace into a suitable receptacle. Some of the lead is blown by the blast of air into fume, and is more or less oxidised to oxide and sulphate during that operation; this fume

passes up into the collecting hood which is placed above the hearth, and from thence into a large chamber, where it collects on the sides. These chambers are built in two storeys of brick and iron, the openings connecting the two storeys are covered by means of woollen bags; a powerful fan in the second storey draws the gases produced during the process of furnacing through the bags, but the latter retain the lead fume, which therefore collects in the lower storey of the chamber. The woollen bags are shaken from time to time to dislodge the fume which collects on them. At intervals the fume in the lower storey is set fire to, a proceeding which completes the oxidation of the lead fume, and, at the same time, makes the fume more consolidated, and, therefore, better for use as a pigment. The burnt fume has a lead colour, and requires further treatment before it can be used as a white pigment, although it is sold in this state as a lead-grey colour.

The next operation, in which the pigment is made white, takes place in the "slag-eye furnace" as it is called. This slag furnace consists of a square brick chimney, fitted with a hearth, tuyeres, and water back. In this furnace the fume from the last operation is heated in a powerful blast of hot air, which causes most of it to become completely oxidised to lead sulphate, which passes into condensing chambers, where it collects. These chambers are constructed in exactly the same way as those described above. As a rule, the pigment is ready for sale, but occasionally it may have a slight grey colour; to get rid of this it is treated with sulphuric acid, which causes it to whiten, and sometimes it is ground in order to render it as fine as possible.

Sublimed white lead is a powder of a fine white colour, although sometimes it has a grey tint; the white has a rather bluish hue. It is heavy, its specific gravity being over 6; a cubic foot weighs about 200 lbs. It is quite insoluble in water, is partially soluble in dilute nitric acid, which dissolves out the zinc oxide, lead oxide, or lead carbonate the pigment may contain; as a rule, it is completely soluble in boiling hydrochloric acid, although some samples contain a little barytes, which remains behind as an insoluble residue on treatment with the acid.

In composition it is very variable. Much depends upon the ore from which it is made, and whether anything has been added to it after the pigment was made in the furnaces described above. The following analyses are partly from published accounts, and partly from the author's own results:—

	I.	II.	
Lead sulphate, $PbS O_4$, . . .	70	82.390	per cent.
Lead oxide, PbO , . . .	23	0.554	„
Zinc oxide, ZnO , . . .	7	6.335	„
Lead carbonate, $PbCO_3$,	9.421	„
Water, hygroscopic,	0.350	„
Water, combined,	1.050	„

The proportion of oxide of zinc and sulphate of lead contained in the pigment is, to some extent, a measure of the value of the pigment for painting purposes.

Sublimed white lead when well made is a fairly satisfactory pigment. It possesses good colouring power and body or covering power, although in this respect it is perhaps not quite equal to the best white lead. It is more permanent than white lead, because sulphureous gases and vapours have little or no action upon it; it, therefore, keeps its colour longer when used in paint and exposed to air. Being insoluble in water and acids it is not so poisonous as white lead.

It has been noticed that occasionally when mixed with oil and turps, sublimed white lead has a tendency to become gelatinous; on what this peculiar property depends is somewhat uncertain.

FREEMAN'S NON-POISONOUS WHITE LEAD.

The base of this white lead is the sulphate made from metallic lead by precipitation, it also contains zinc oxide, barytes, and, in the earlier makes, a little magnesia, all the ingredients being mixed together by a process of grinding under edge runners, which causes them to be thoroughly incorporated together, and, at the same time, by consolidating the materials, increases the body or covering power. The pigment was first patented in 1882, but since then other patents have been taken out for improvements in its composition, which, in consequence, has varied a little from time to time. The non-poisonous white lead is a very good pigment, is more permanent under exposure to atmospheric influences than white lead, and is equal to white lead in body or covering power and in freedom of working. It is rather heavier than white lead, weighing about 180 to 190 lbs. to the cubic foot. Its specific gravity is 5.95 to 6.00. It is one of the best substitutes for white lead which have been made.

HANNAY'S CALEDONIAN WHITE LEAD.

Messrs. Andrew French & J. B. Hannay in 1884 took out a patent for the preparation of a chloro-sulphite of lead to be used

as a substitute for white lead. This was an extension of a former process of French's for the production of a sulphite of lead pigment (see p. 53).

To prepare the chloro-sulphite of lead, lead ore, lead-fume, or any lead compound is mixed with coke, and, if the amount of sulphur in the ore or lead used is deficient, with some pyrites, as it is necessary that a large quantity of sulphurous acid (sulphur dioxide) gas should be produced. This mixture is placed in a kind of cupola furnace provided with an air blast. The heating of the furnace and the amount of air blown through is to be so arranged that the lead is oxidised to sulphite, not to sulphate; the sulphite is carried by the blast into a chamber and along flues where it comes into contact with hydrochloric acid gas, which, by its action on it, produces the chloro-sulphite. The hydrochloric acid gas is formed by sending a solution of salt into the flues in the form of a fine spray; the sulphurous acid in the furnace gases acting on the salt under such conditions decomposes it into hydrochloric acid and sulphite of sodium. From the flues the pigment is carried into large condensing chambers where it collects; from time to time the chambers are emptied of their contents, and the pigment washed with water and dried, when it is ready for use.

In a subsequent patent Mr. Hannay describes the production of the sulphate of lead from lead-fume, &c., by heating in a cupola furnace with a blast of air. The fume which is thus produced is carried through a kind of reverberatory chamber, where it is completely oxidised to sulphate; this is carried forward by the draught into large chambers where it collects. If white enough the pigment so obtained is sent out for use; if it has a grey colour due to the presence of metallic lead it is bleached by treatment with an acid. To improve the quality of the pigment it may be mixed with zinc oxide.

One difficulty which is met with in all these subliming processes is that of collecting the lead-fume or pigment. This necessitates the use of large condensation chambers or long flues to ensure the complete deposition of the material, or otherwise there is great risk of much of the material being carried forward by the draught into the chimney of the works and so out into the atmosphere where it is lost.

To provide these large chambers or long flues is not always possible, both on account of the cost of construction and of the space they require. To remedy this, Mr. Hannay has devised a special form of condenser constructed as follows:—A large closed chamber made of iron is partially filled with water, the flue from

the furnace passes through the top of the chamber and terminates a little below the surface of the water, so that all the gases from the furnace must pass through the water. On each side of the flue in the water is arranged a number of metallic gauze screens in such a way that the gases, &c., must pass through them on their way from the flue. These screens serve to collect the fume and solid matter which comes from the furnace; from time to time the screens are shaken by the mechanical contrivance provided for that purpose, which frees them from the fume that has deposited upon them and this settles down to the bottom of the tank or water chamber. The flue gases which pass through the screens are drawn through them and the water into a chimney by means of a fan. From time to time the fume that deposits is collected and treated as may be required to convert it into a useful pigment.

The properties of the pigment thus made do not differ much from those of the sublimed white lead described above.

MAXWELL LYTE WHITE LEAD.

In 1886, Mr. Maxwell Lyte patented the production of a basic sulphate of lead for use as a pigment. The process of manufacture is given as follows:—A solution of basic acetate of lead is made by pouring three-fourths of a solution of the normal acetate of lead of a specific gravity of 1.15, 30° Tw., over spongy lead, by which means a solution of basic acetate, having a specific gravity of 1.315, or 63° Tw., is obtained. 100 gallons of this solution are taken, and to it is added just enough sulphuric acid to turn litmus paper red; the mass is then boiled, the sulphate allowed to settle, and the clear liquor used for making new solutions of lead. The precipitate of lead sulphate obtained is then treated with a solution of basic acetate of lead, being boiled therewith for an hour, when the basic sulphate will be formed.

The sulphate of lead pigments may be distinguished by boiling them with hydrochloric acid, which will, if free from barytes, dissolve them completely; any barytes they may contain will be left as an insoluble residue. The solution will yield a white precipitate of barium sulphate on adding a solution of barium chloride, and will deposit crystals of lead chloride on cooling. The presence of lead carbonate, zinc oxide, or other white pigments, may be detected in either a nitric acid or hydrochloric acid solution by the tests given under white lead.

A full analysis of these lead sulphate pigments is rarely re-

quired; but they should be assayed for colour, hue, covering power, &c., by the methods described in another chapter.

SULPHITE OF LEAD WHITE.

Sulphite of lead is a white insoluble powder containing lead oxide and sulphur dioxide, and having the formula $PbSO_3$. It was first proposed to be used as a pigment in 1850 by *Dr. John Scoffern*, who took out a patent for its production and use for painting. The process he describes for its preparation is to prepare a solution of basic acetate of lead, and to precipitate the sulphite from this by passing a current of sulphur dioxide gas through it. A solution of normal acetate is left, which may be used for preparing fresh basic acetate; while the pigment which is precipitated is collected, washed with water, and dried. This sulphite white is said to be of good colour and body, to mix better with oil than the sulphate, and to keep its colour better than the carbonate white.

In 1881 *Andrew French* patented a process of manufacturing a white pigment, which consisted of a mixture of about 80 per cent. of sulphite of lead, with 20 per cent. of oxide of zinc, although these proportions were liable to vary from time to time. This pigment was made by mixing ores containing both lead and zinc with carbon in such forms as coal, charcoal, coke, &c., and treating the mixture in a low cupola furnace fitted with a hot blast. By this treatment the ore becomes partly reduced to the metallic state; while some is oxidised and carried by the blast of air in the form of fume into flues and collecting chambers, where it settles out. The amount of air supplied in the blast is so arranged that the oxidation is limited, and the sulphites of the metals are produced and not the sulphates (see *Sublimed and Hannay's white leads*). The pigment so made is described as being superior to ordinary white lead, inasmuch as it retains its colour longer and is superior to sulphate whites in having more covering power or body, and mixing with oil better.

The author has not seen any of these sulphite whites, and they are not now made.

ZINC WHITES.

Several white pigments containing zinc as their base are now used as pigments on a fairly large scale. These usually contain as their essential constituent one or other or both of two compounds of zinc—viz., the oxide, ZnO , and the sulphide, ZnS ;

the former has been used as a pigment for a long time, the latter is of comparatively recent introduction. The oxide is generally sold under the name of zinc white, and is always the body or compound which is understood to be designated by that term. The sulphide is rarely sold pure, but is more or less mixed with oxide of zinc and other white pigments, and sold under a variety of names, which will be given below.

ZINC WHITE.

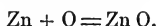
This pigment, also known as Chinese white, consists entirely of the oxide of the metal zinc, which has the composition—

Zinc, Zn,	.	.	.	80.25	per cent.
Oxygen, O,	.	.	.	19.75	„

having the formula ZnO .

It can be prepared in two ways—

1. *By Combustion of Metallic Zinc.*—Zinc is a volatile metal, and when heated to a white heat it is readily converted into vapour; if this comes into contact with air or oxygen combustion can take place, and the oxide is formed by the union of the metal with oxygen, as shown in the equation—



The usual method of manufacturing zinc white is based on this reaction.

2. *By the Action of Heat on certain Zinc Compounds.*—When the carbonate or hydroxide of zinc are heated strongly they lose part of their constituents, leaving a residue of oxide behind. This method of preparing zinc white has been used and made the subject of many patents.

1. **Combustion Method.**—This is the principal method for preparing zinc white. The process is carried out in a special form of plant, which is shown in Figs. 8 and 9. This plant consists essentially of two portions, one in which the zinc is produced in the form of vapour, and the other of chambers in which the white formed by the combustion of the zinc vapour is collected. The vapourising plant consists of a furnace, A A, in which are placed a number of fireclay retorts, B B B. These furnaces are made double, back to back, so as to accommodate two sets of retorts, as shown in the drawing; they are of the reverberatory type. The retorts are made of fireclay; the usual form is shown in the drawings, although it varies a little at different works. The mouths of these retorts open into a kind of com-

bustion chamber or flue made of sheet-iron; one end of this flue is made funnel-shaped, and is open to the air, so that a current of air can pass through it, the other end of the flue opens into the first collecting chamber. The white hot vapour of zinc,

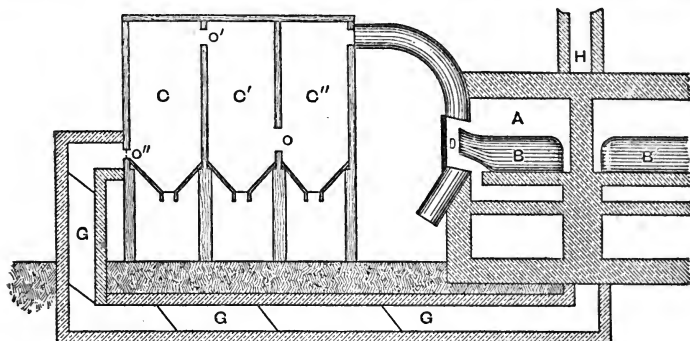


Fig. 8.—Zinc white furnaces.

when it comes from the retort into this flue, burns, and vapour of zinc oxide is emitted in large volumes; this is carried by the draught into the collecting chambers. The collecting chambers, C C C, are large chambers varying in number at different works,

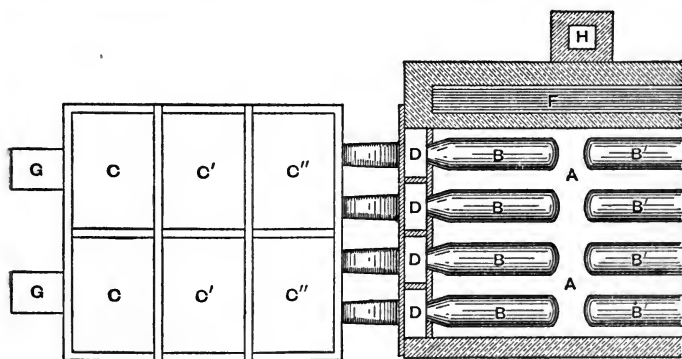


Fig. 9.—Zinc white furnaces.

but usually six set in two series are employed. They are constructed of wood, and each chamber is complete in itself; it communicates with its neighbours on either side by means of small

apertures so placed alternately at top and bottom that the vapours and gases from the retorts must take a circuitous course through the series of chambers; in so doing the oxide of zinc which they carry with them is deposited on the sides of the chambers; finally, the gases pass through a long flue, G G G, to the chimney of the works. In this flue there are screens which serve to intercept any oxide which has escaped condensing in the chambers. The bottom of the chambers is made hopper-shaped, so that, by placing barrels underneath and opening a slide, the oxide can be taken out of the chambers with ease. Although zinc-white chambers are usually constructed of the form shown in Figs. 8 and 9, yet it is obvious that any other form of collecting chambers may be used, such as, for instance, those described under lamp-black.

The retorts measure about 28 inches long by 10 inches broad, and 6 to 8 inches high, the sides having a thickness of $1\frac{1}{2}$ inches. Eight of these retorts are placed in a furnace arranged in two sets of four, back to back; two retorts open into one series of three collecting chambers.

The furnace is so constructed that the flames from the fireplace first pass over the retorts, then under them in a flue, and finally pass out, or rather the products of combustion pass out, into a chimney by the flue, G G G, connected with the collecting chambers, whereby the draught necessary for drawing the zinc oxide through the chambers is created. The draught should be good, so as to ensure a plentiful supply of air to the vapour of the zinc as it passes out of the retorts, otherwise some of the zinc is sure to escape combustion, and this, passing into the chambers unchanged, causes the discolouration of the white.

Usually metallic zinc is used as the raw material for the preparation of the zinc white, but it has been proposed to use zinc ores, such as calamine (carbonate of zinc), and zinc blende, or black Jack (sulphide of zinc), and any products containing zinc, which, by being heated in a retort, can be reduced to the metal, which, being volatilised in the operation, can be burnt and collected in the manner described above. The great objection to this method of procedure is that the zinc ores are rarely pure, being accompanied by varying quantities of other metals—cadmium, antimony, &c. Some of these are volatile like zinc, and on burning form oxides which pass into the collecting chambers and contaminate the zinc white, spoiling the colour very considerably. This is especially the case with cadmium, which is a very common constituent of zinc ores. This metal forms a brown oxide, which, if present, always spoils the zinc white. In the ordinary process of zinc smelting it is eliminated by taking advantage of its greater

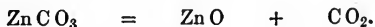
volatility, but it is obvious that in zinc-white making it is not possible to separate it out from the finished product. It is chiefly on account of the presence of these impurities in the zinc ores, and the discolouring action they have on the white, that they are not now used for preparing it.

Occasionally it is found that the white collected in the first chambers is not so good as that collected in the following ones; this is due to the presence of small traces of impurities in the zinc which is used and which it is difficult to entirely eliminate. These impurities are found to collect mostly in the first chamber, and the white in this is, when found to be of a poor colour, sold as an inferior quality of zinc white.

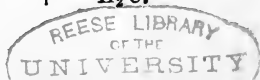
The general methods of working is to raise the retorts to a white heat, and then to throw in the ingots of zinc; all apertures are now closed up excepting those leading from the air to the combustion chamber and into the collecting chambers. The zinc soon begins to volatilise, and on issuing from the mouth of the retort burns. It is essential to prevent the combustion taking place within the retort because it would then soon become choked up by a deposit of infusible oxide. This can only be done by making the mouth of the retort narrow, and scraping the crust formed on the mouth of the retort by means of scrapers. The zinc white formed by the combustion of the vapours is of two kinds, light and heavy; the former passes into the chambers and is there collected, the latter drops down the combustion chamber, being rather heavy, into a barrel placed for its reception, and being usually of a poor colour, may be returned to the retorts with the next batch, along with a small quantity of carbon in some form or other.

The zinc white made by this process, while being of a good colour, is very light and, in consequence, is rather deficient in body, still it gives a more uniform product than any other process hitherto devised, and is, therefore, the chief, if not the only, process now in use for making zinc white.

2. Ignition Methods.—When carbonate of zinc, ZnCO_3 , is heated it loses its carbonic acid and leaves a residue of zinc oxide, ZnO , according to the equation—



Similarly the hydroxide, ZnH_2O_2 , loses water and leaves oxide behind—



Other salts of zinc, such as the nitrate ($Zn\ 2\ N\ O_3$), the sulphate ($Zn\ S\ O_4$), the sulphide ($Zn\ S$), are also altered when heated and yield a residue of oxide; but they require rather a higher temperature to effect their decomposition than do the first two compounds named.

Neither of these two compounds occurs naturally in a sufficiently pure form to be used as a source for the preparation of zinc white by an ignition method, therefore they have to be prepared artificially; the carbonate, by precipitating, by means of a solution of sodium carbonate, any solution of zinc, when it is obtained as a white powder insoluble in water. The hydroxide is similarly obtained by adding a solution of caustic soda to a solution of zinc. In this case care has to be taken not to add the precipitant in excess or otherwise some of the hydroxide first thrown down will be redissolved again, zinc hydroxide being soluble in caustic soda solution. The precipitates in either case are well washed with water by decantation, and then drained on a filter. It is not necessary to dry them. When as much water has drained from them as possible, the mass is thrown into a crucible and heated to a white heat for some time, when a bright yellow residue of zinc oxide is left in the hot crucible; this, however, as it cools turns white. When cold the oxide is ground up for use as a pigment. The white obtained by this process is a good one, has good body or covering power and is of good colour; but the process of manufacture is more costly than that by combustion, consequently, it is rarely, if ever, used. Attempts have been made to utilise by this method many waste solutions of zinc which are obtained in various industries, but hitherto without much success. The principal difficulties are the trouble of collecting these liquors and the influence which any impurities they contain may have on the colour of the resulting pigment, these impurities being difficult, if not impossible, to eliminate by any practicable process.

PROPERTIES OF ZINC WHITE.

Zinc white is a rather bulky fine white powder, having a specific gravity of 5.6. In hue it is rather bluish. It is quite insoluble in water, oil, alcohol, and turpentine. It dissolves in dilute sulphuric acid, hydrochloric acid, acetic acid, and many other acids without effervescence, giving colourless solutions. It is also soluble in ammonia and alkaline solutions. It is unchanged by exposure to air and light, and sulphur

or sulphur gases have no visible action on it, as the sulphide formed is white like the oxide; as a pigment, therefore, it is quite permanent. It mixes well with all vehicles used in preparing paints. For preparing the stiff paste, which is sometimes sold, it requires about 22 per cent. of linseed oil, a much larger proportion than is required by any other pigment. It mixes well with water, and in this form it is largely used by water-colour artists, under the name of Chinese white. It can be mixed with all other pigments without undergoing any change or changing the other pigment. The chief fault of zinc white is its want of body or covering power. This is, no doubt, due to its bulkiness, which is inseparable from the mode of preparation. Many attempts have been made to produce a dense zinc white. The plan most commonly in use is to grind the pigment for some time under edge runners, so as to break down, so to speak, the voluminous character of the pigment, and make it more powdery, in which form it has greater covering power. Another proposed plan is to heat the zinc white to a red heat, and then drop it into cold water; the sudden cooling effects the breaking up of the particles of zinc white, but this method is not so effective as the grinding process, and is rather more troublesome to carry out. This want of body, coupled with the fact that it is rather costly, has limited the use of zinc white much below that justified by its permanent qualities.

ASSAY AND ANALYSIS OF ZINC WHITE.

Zinc white can be assayed for covering power and colour in the usual way.

Zinc white, being a rather costly pigment, is very liable to adulteration with other white pigments, such as china clay, barytes, whiting, terra alba, &c.

Zinc white should be completely soluble in dilute sulphuric acid without effervescence; a property possessed by no other white pigment. Effervescence indicates an addition of white lead, whiting, or magnesite. Most other adulterants are left as an insoluble residue. The solution in acids is quite colourless. On adding ammonia, a white precipitate is first obtained; but, on adding an excess, this is redissolved; any lead, if present, is left as an insoluble residue. On adding ammonium sulphide to the ammoniacal solution, a white precipitate of zinc sulphide will be obtained; this precipitate should be quite white, or, at most, have a faint yellow tint, due to its containing traces of the yellow ammonium sulphide; any other colour would indicate

impurities. This precipitate should be filtered off, and to the filtrate a solution of ammonium oxalate be added; no precipitate should be obtained; if there is any it indicates the addition either of calcium carbonate in the form of whiting (which is also indicated by effervescence with acids), or of calcium sulphate. If to the solution or filtrate from the ammonium oxalate sodium phosphate be added, the formation of a white precipitate indicates the addition of magnesium.

If a preliminary test with dilute sulphuric acid shows that adulterants are present, it will be best to treat the pigment with hydrochloric acid, and boil it, filtering off any insoluble residue, and then allowing the solution to cool; if crystals form, then lead is present, and has been added either in the form of white lead or lead sulphate, the character of the results obtained will indicate which. In the solution zinc, calcium, and magnesium may be looked for as described above. If an insoluble residue is left it may contain barytes, china clay, or gypsum, which substances may be tested for in the way described under their respective heads.

The quantity of zinc oxide in a pigment can be thus ascertained—Weigh out about 1 gramme of the pigment, dissolve it in hydrochloric acid, and to the solution add first ammonia in excess, then ammonium sulphide in slight excess; the mixture is placed on one side for a few hours, and then filtered; the precipitate of zinc sulphide is well washed, dried, placed in a porcelain crucible, and ignited at a bright red heat, taking care that plenty of air reaches the material in the crucible; by this means the sulphide is converted into oxide. When the reaction is considered to be complete, the crucible and its contents are allowed to cool, and, when cold, are weighed; the weight of zinc oxide found gives at once the weight of zinc white in the pigment.

SULPHIDE OF ZINC WHITES.

When ammonium sulphide is added to alkaline solutions of zinc salts, or when sulphuretted hydrogen is passed through similar solutions, a white precipitate of the sulphide of zinc is obtained. This is a body composed of sulphur and zinc in the following proportions—

Zinc,	67	per cent.
Sulphur,	33	„

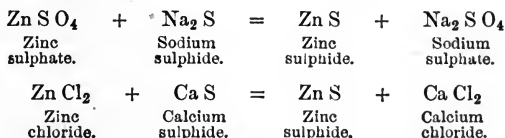
its formula being $Zn S$.

The first mention of the use of this compound as a pigment

occurs in a patent granted in 1852, the process for its preparation being to add a solution of sulphide of potash to one of zinc sulphate. The patentee did not prepare it with a view of using it as a painters' pigment, but for the purpose of colouring india-rubber.

During the last twenty years very considerable attention has been paid to zinc sulphide as the possible base of a white pigment. The consequence has been that it is now manufactured on a large scale by several colour manufacturers and sold as a pigment under a variety of names, as Orr's Charlton white, Orr's enamel white, Griffith's patent zinc white, patent zinc white, lithophone, &c. None of these bodies consist only of sulphide of zinc, but contain oxide of zinc, barytes, magnesia, &c.

When alkaline sulphides are added to solutions of zinc salts, a white precipitate of the sulphide is obtained, according to the equations—

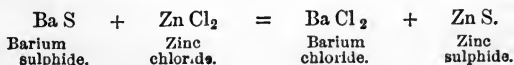


which may be considered as typical of the operations carried out on a large scale.

Zinc sulphite possesses what to the painter is of great importance, "body;" the colour is apt not to be good. It is extremely difficult to remedy this defect with pure zinc sulphide, but by introducing other bodies and preparing the sulphide in a special way, a pigment possessing both good colour and good body may be obtained.

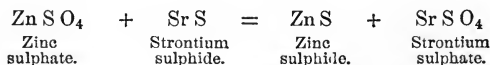
ORR'S WHITE ENAMEL OR CHARLTON WHITE.

This zinc pigment was first patented in 1874, and is the parent of this group of zinc whites. The process of manufacture consists in first preparing barium sulphide by calcining barytes with charcoal for some hours at a white heat; the calcined mass is then lixiviated with water to dissolve out the barium sulphide which is formed. The solution so obtained is divided into two equal portions. To one of these is added a solution of zinc chloride, whereby a precipitate of zinc sulphide is obtained according to the equation—



The precipitate is not separated, but to the mass is now added the rest of the barium sulphide and sufficient solution of zinc sulphate, when a combined precipitate of zinc sulphide and barium sulphate will be obtained. This precipitate is washed with water, filter-pressed, dried, and then calcined at a red heat in a suitable furnace. While still hot the mass is thrown into cold water, which causes it to become rather denser than it otherwise would be, and thus have more body; the product is finally ground as fine as possible and dried, when it is ready for use. The calcination causes some of the zinc sulphide to become converted into oxide, and thus the final product will consist of a mixture, more or less intimately united, of zinc sulphide, zinc oxide, and barium sulphate. It is quite possible that the zinc compounds are in a state of more intimate union than would be the case if they were simply prepared separately and then mixed together; that, in fact, an oxysulphide of zinc is formed. The exact composition of the pigment will depend upon several factors, the proportion between the barium and zinc salts used may be varied, while the duration of the calcination will influence the result by increasing the proportion of oxide in the pigment.

In a later patent Orr describes a similar process, but the materials used are zinc sulphate and strontium sulphide. The patentee proposes to make the zinc sulphate by slightly calcining poor ores of zinc in such a way that the sulphate is formed; the calcined mass is lixiviated with water in such a way that a solution of 1.150 specific gravity is obtained. The strontium sulphide is prepared by calcining celestine (natural strontium sulphate) with charcoal; the calcined mass on lixiviation with water yields a solution of strontium sulphide of specific gravity 1.060. These two solutions are mixed in equivalent proportions when a combined precipitate of zinc sulphide and strontium sulphate is obtained, as shown in the following equation:—



This precipitate is washed, dried, and calcined as above. The resulting pigment is a combination of zinc sulphide, zinc oxide, and strontium sulphate. The patentee specifies that the calcination shall be continued until all sulphur vapours are given off. The white pigment so obtained is described as being equal in body to white lead, while it possesses the merit of not being discoloured by sulphuretted hydrogen.

Charlton white is an excellent substitute for white lead; its

colour is good, its body is nearly equal to that of white lead, while it possesses the advantages of not being discoloured by sulphuretted hydrogen, by sulphur gases or pigments, and of being non-poisonous. It mixes well with all vehicles, so that it may be used for all kinds of painting with good results. It mixes with all pigments except those having lead or copper as their base; these it is liable to discolour on account of the sulphur it contains, but with any other pigments there is no change produced on mixing.

GRIFFITH'S PATENT ZINC WHITE

was introduced about 1876, and is made under a patent dated 1875. The process of manufacture consists in taking "vat waste," a residue of the Leblanc process of alkali-making and exposing it to the oxidising action of the atmosphere for some time; after which it is lixiviated with water, and a solution, consisting largely of calcium sulphide, with some sodium sulphide, obtained. To this solution an equivalent quantity of a solution of zinc sulphate is added, when a precipitate of zinc sulphide, along with some calcium sulphate, is obtained. Barium sulphate, in a state of fine division, is prepared by adding a solution of barium chloride to one of magnesium sulphate. The zinc sulphide and barium sulphate are now mixed together, and, after being dried, are calcined until no further vapours are given off; the calcined mass is then ground with water, levigated, and dried, when it is ready for use.

Another method of making this white is to mix together solutions of barium chloride and zinc sulphate, when barium sulphate is thrown down; to the mixture is now added the "vat waste" liquor as before, which precipitates zinc sulphide. The two compounds are thus obtained in a much better state of admixture than is the case when made according to the last process. The mixture is calcined as above. The best precipitating agent is said to be "pentathionide of calcium," prepared by boiling 65 parts of sulphur with 35 parts of calcium sulphide in the state of solution, when a red liquor is obtained, which can be used to precipitate the zinc salts.

A dry method of preparing the white consists in mixing 2 parts of barium sulphate with 1 part of zinc oxide and 10 per cent. of sulphur and 5 per cent. of sodium carbonate; this mixture is calcined, levigated, and dried.

A somewhat different process, one more on the lines of Orr's patent, is described in a subsequent patent, taken out in 1877

by *Griffith*. According to this, barium sulphide is prepared by calcining barytes with charcoal, and a solution is obtained by lixiviation in the usual way; to this is added an equivalent quantity of a solution of zinc sulphate, when a precipitate, consisting of a mixture of barium sulphate and zinc sulphide, is obtained. This is calcined in crucibles, without air being admitted, so that very little, if any, oxidation takes place; the calcined mass is ground with water, and, after being washed, is dried and mixed with a small quantity of magnesia, which imparts to it the property of more thoroughly mixing with oil, and gives it a softness in working which it would not otherwise have.

In the preparation of zinc sulphide whites, one difficulty which is encountered is that the product sometimes comes from the calcining furnace with a yellow tint; this, perhaps, is due to oxidation, which must be avoided. For this purpose *Griffith* mixes the mass, before calcining, with from $\frac{1}{2}$ to $2\frac{1}{2}$ per cent. of ammonium chloride or ammonium sulphate, which, by being volatile, produces an atmosphere of ammonia round the pigment, thereby preventing oxidation and the discolouration of the pigment.

A rather novel method of preparing sulphide of zinc was patented by *Griffith & Cawley* in 1879. The principle of this method lies in the fact that when zinc and sulphur are brought together, in the state of vapour, they will combine to form the sulphide. The process is carried out in the plant shown in

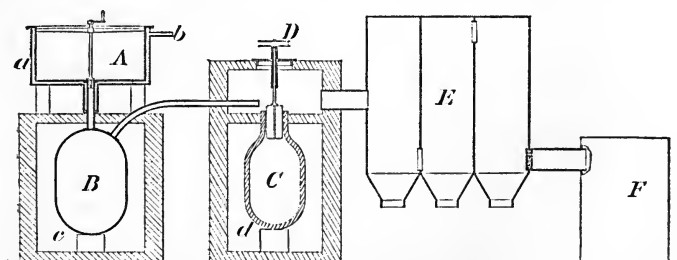


Fig. 10.-- Zinc sulphide white plant.

Fig.10. Sulphur is placed in the vessel, A, where it is melted; it flows into the egg-shaped still, B, contained in the furnace, G, in which it is converted into vapour; the zinc vapour passes into another chamber, where it comes into contact with vapour of metallic zinc from the still, C; the two bodies unite to form

sulphide, which passes along into the chambers, E, where it collects. These chambers are constructed similarly to those used in making ordinary zinc white; but they are kept hot, so that any excess of sulphur vapour can pass through them and be collected in the chamber, F. The zinc sulphide which collects in the chamber, E, is ready for use as a pigment, or it can be mixed with barytes, &c. D is a revolving scraper, for the purpose of keeping the mouth of the zinc still free from any deposit of sulphide which might tend to cause it to become choked up.

Griffith's patent zinc white is very largely used as a pigment; its colour is good, in body it is nearly, if not quite, equal to that of white lead, while it is far superior to that of ordinary zinc white. It does not become discoloured by exposure to sulphuretted hydrogen, or to any other sulphur compounds; it resists exposure to all atmospheric agencies, and is one of the most permanent white pigments known. It mixes well with oil, working very freely under the brush; in this respect it is quite equal to white lead. It mixes with all pigments, excepting those containing lead or copper, without being changed by them, or changing them in any way.

A sample of Griffith's zinc white, analysed by the author, had the following composition:—

Water, hygroscopic,	1·362	per cent.
Water, combined,	3·712	„
Zinc oxide, Zn O,	9·182	„
Zinc sulphide, Zn S,	23·041	„
Barium sulphate, Ba S O ₄ ,	62·541	„

KNIGHT'S PATENT ZINC WHITE.

This zinc white is prepared, according to the patent of 1876, by adding sulphuretted hydrogen or a solution of calcium sulphide or calcium pentasulphide to hot solutions of either zinc chloride or zinc sulphate; the precipitate of zinc sulphide obtained is collected, washed, dried, and calcined. To a mixed solution of zinc sulphate and kieserite, which is crude magnesium sulphate, a solution of sodium carbonate is added, whereby a mixed precipitate of the carbonates of zinc and magnesia is obtained; this, after washing, drying, and calcining, is mixed with the calcined zinc sulphide obtained in the first instance.

The best precipitant for the zinc is said to be calcium pentasulphide prepared by boiling vat-waste liquor with sulphur in such a way that for every 40 parts of calcium there are 160 parts

of sulphur ; a red liquor is obtained which may be used for precipitating the solutions of zinc.

In a patent taken out in 1882 a process of preparing zinc sulphide white is described which is rather more complicated. The process consists in preparing three solutions. No. 1 is a solution of sodium sulphide, obtained by boiling caustic soda with sulphur in the usual way. No. 2 is a solution of zinc sulphate. No. 3 is a solution of strontium chloride prepared by dissolving the carbonate in hydrochloric acid.

Nos. 1 and 2 are mixed in equivalent proportions, whereby there is formed a precipitate of zinc sulphide and a solution of sodium sulphate. To the mixture is now added an equivalent quantity of solution No. 3, when a precipitate of strontium sulphate and a solution of sodium chloride are formed. A precipitate consisting of zinc sulphide and strontium sulphate in equivalent proportions is thus obtained ; this is collected, washed, dried, and calcined. The calcined mass is finished by grinding, levigating with water, and drying.

This white has similar properties to the two whites described above.

Besides the processes described above for making zinc sulphide whites, the following may be mentioned as having been made the subject of patents:—*Parnell* dissolves zinc in alkaline solutions and throws down the sulphide by means of an alkaline sulphide, the pigment being finished by calcining as above. *William's* process does not differ much from that of *Orr* ; he takes a solution of zinc chloride and throws down the sulphide by means of a solution of calcium sulphide ; after separating the solution of calcium chloride which is formed, a solution of barium chloride is added and then one of sodium sulphate ; the combined precipitate of zinc sulphide and barium sulphate is then finished by calcining ; sometimes a little magnesia is added to enable the pigment to mix with oil more perfectly. *Claus* dissolves zinc carbonate (either the natural variety calamine, or the artificial product) in ammonia ; to this is added a solution of barium sulphide which throws down a precipitate of zinc sulphide and barium carbonate. This precipitate is collected, dried, and calcined out of contact with air ; while still red hot the calcined mass is thrown into cold water, then ground, levigated with water, and dried. The use of the waste liquors of galvanisers is mentioned as a source of the zinc solution by *Claus* in his patent specification.

One of the difficulties met with in the preparation of the zinc whites just noted is that they are very liable to turn yellow

during the process of calcining, which yellow tint is preserved in the finished product. This yellow tint is obviously objectionable and is probably due to over-oxidation. Several remedies have been proposed to avoid this defect. One of these is to calcine without exposure to the air so that oxidation cannot take place; another remedy is described in the notice of Griffith's white; still another is not to wash completely the precipitate, but to leave a little of the soluble salts in it which tend to preserve the purity of the colour.

The defect is not so prominent when the pigment is made as proposed by *Knight*, by mixing 1 part of zinc sulphide with 2 to 3 parts of zinc oxide and 4 or 5 parts of barytes with a little magnesia; this mixture is calcined out of contact with the air, so that there is little or no discolouration; still this method does not give as good results as the other processes which have been described.

ASSAY AND ANALYSIS OF ZINC SULPHIDE WHITES.

As these are of such variable composition it is necessary to assay them for colour and covering power in the usual way.

An analysis of these whites is rarely required. When such is the case, the analysis of Griffith's white given above, and that of the lithophone which is given below, will show what to look for in these whites.

They are distinguished from other white pigments by being partially soluble in hydrochloric acid, sulphuretted hydrogen being given off during the solution of the pigment in the acid.

The solution in hydrochloric acid will show the characteristic tests for zinc given under zinc white, and will contain any magnesia which may have been added to the white, as also any calcium which may be present. If the white has been made with barium or strontium carbonates, the solution will also contain barium or strontium; these may be tested for by adding sulphuric acid, when, if present, a white precipitate of the sulphates will be obtained, and can be differentiated by applying the distinguishing tests.

The residue which is left undissolved, on treatment with hydrochloric acid, will consist of either sulphate of barium or sulphate of strontium; these may be distinguished by using the flame tests.

A sample of lithophone, one of the zinc sulphide whites examined by the author, had the following composition:—

Barium sulphate, $BaSO_4$,	. . .	67.96 per cent.
Zinc oxide, ZnO ,	. . .	7.32 „
Zinc sulphide, ZnS ,	. . .	24.85 „

This pigment possessed a good body and worked well in oil ; it had a slight yellow tint.

BARYTES.

Barytes is one of the most important white pigments at the disposal of the painter ; probably, in this respect, ranking next to white lead, both as to the extent of its use and to its qualities as a pigment. In composition it is the sulphate of the metal barium and is obtained from both natural and artificial sources. The composition is indicated by the formula $BaSO_4$. Naturally, it occurs in large quantities very widely distributed, forming the mineral barytes, heavy spar, or, as it is called by the lead miners, cawk. Artificially, it is obtained whenever sulphuric acid or solution of a sulphate is added to a solution of a barium salt.

In this country barytes is found most abundantly in Derbyshire ; while in Cornwall, Devonshire, Cumberland, several places in Wales and Ireland, it is also found and worked. It occurs in the form of large crystalline masses, generally opaque, but sometimes transparent pieces are found ; in some cases the crystalline character is not very strongly developed and then the barytes appears to be more or less amorphous. The normal colour of the barytes is white, but often it has a faint yellow tint, due to the presence of small quantities of oxide of iron ; it often has small streaks of lead ore (galena) distributed throughout its mass.

The following analyses of two samples of Derbyshire barytes will show the average composition of this mineral :—

	Opaque variety.	Crystalline variety.
Specific gravity,	4.112	5.02
Barium sulphate, $BaSO_4$,	98.796	98.566
Ferric oxide, Fe_2O_3 ,211	.830
Calcium sulphate, $CaSO_4$,767	.504
Magnesia, MgO ,	trace	.017

As a rule the transparent variety is heavier than the opaque variety, as is seen from the above analyses. Of two samples of Cumberland barytes, one, a transparent variety, had a specific gravity of 4.5, while the other, an opaque sample, had a specific gravity of 4.3.

PREPARATION OF BARYTES.

In principle the preparation of barytes as a pigment is very simple. It merely requires grinding to a fine powder, when it is ready for use. In practice, however, to ensure the best results a little more than this is required. The crude barytes comes to the grinder in large lumps more or less contaminated with foreign minerals; the crude material is first hand-picked to separate out all pieces that are not barytes and in some cases to pick out the small pieces of lead ore with which the mineral may be mixed. The subsequent treatment varies a little at different barytes works, according to the character of the machinery which is available, but the following may be taken as a description of the general method in use for preparing barytes:—After being picked, the pieces or lumps of barytes are ground to a coarse powder under edge-runner mills; from these it is transferred to flatstone mills, in which it is further ground, usually under water, a constant stream of which is caused to pass through the mills during the operation; from these mills the ground barytes is passed to settling tanks, which are usually constructed of stone; in them the barytes settles in a few hours, the supernatant water is run away, while the top portion of the mass of barytes, being the finest, is taken and stored ready for the next operation; while the bottom portion, which is usually much coarser, is sent back into the grinding mills again to be re-ground. The grinding cannot be too well done as on it depends the quality of the resulting pigment.

After the grinding the barytes is next subjected to a bleaching process to free it from any yellow tint it may possess. This tint is due, in almost all cases, to oxide of iron, from which barytes is rarely free. The process is carried out in stone cisterns, the size of which will vary in different works according to the quantity of barytes it is desired to treat at one time; a steam pipe is fitted to the cistern, so that the contents may be heated, an operation which facilitates the bleaching. The wet barytes from the settling tanks is run into these stone cisterns, and heated up to near the boiling point; then a quantity of hydrochloric acid is run into the cistern, the amount used varying considerably. As a matter of fact it should be proportioned to the amount of oxide of iron in the crude barytes, but, as a rule, it is added in a rule of thumb sort of way at most works; on an average about 1 cwt. of acid to 1 ton of crude barytes is used.

The acid extracts the oxide of iron, leaving the barytes quite

white. Hydrochloric acid is the best to use for bleaching barytes, because it has most solvent action on the oxide of iron, and because it is cheap; if the barytes contains any carbonate this will be dissolved by the acid, but may be recovered by adding sufficient sulphuric acid to the solution to precipitate all the dissolved carbonate as sulphate; it is doubtful whether the gain of barytes thus obtained is worth the expense.

It is a good plan to give the barytes two treatments with the acid, using the second acid from one batch for the first acid treatment of a second batch of barytes, the second treatment being with fresh acid, which is used afterwards as the first acid for another batch; the acid which has been used for two lots of barytes may then be thrown away. Working in this way a smaller quantity of acid is used, while the barytes is better bleached; because the second lot of acid, being fresh and strong, has a better chance of dissolving out the last traces of oxide of iron than acid which is already spent and charged with that body.

After treatment with acid the barytes is allowed to stand to settle, the acid liquor is poured off, and water is poured on to wash the barytes; this washing being repeated once or twice so as to wash all traces of acid out of the barytes. This is now in some works subjected to a levigating process to obtain as fine a quality of barytes as possible, the coarser qualities being sent back into the grinding mills to be reground. It takes about three hours for barytes to settle out of the wash waters in the settling tanks which are used, the clear water is syphoned or drawn off in any convenient way, and the barytes, which is in the form of a stiff paste containing some 25 to 30 per cent. of water, is passed on to the drying stoves to be dried.

The drying of the wet barytes is generally done in two stages. From the settling tanks the barytes is thrown on to the tops of drying flues, which flues are horizontal and run round three sides of a drying shed, and are connected at one end with a furnace or fire-place, at the other with a chimney. The flues are about 2 feet 6 inches square, the sides being built of brick, while the top is formed of flagstones. On the top or tops of the flues the wet barytes is thrown, and it is allowed to remain until it becomes sufficiently dry to adhere together; when it has reached this condition it is cut up into large bricks. The bricks are now transferred to the drying stoves. The drying stoves are large chambers built of brick; in the centre is built a furnace which is so constructed that it may be fed from the outside. In some works there is built in the centre of the chamber a large globular shaped vessel of iron which is in connection with the furnace, so

that it may be heated to a red heat ; this vessel, generally known as "the balloon," adds considerably to the temperature and, therefore, to the drying power of the stove. Over the furnace and balloon, and around the sides of the stove, are built ranges of skeleton shelves of iron, on which is placed the bricks of barytes taken from the tops of the drying flues, and where they are allowed to remain until they get properly dry, which takes several days ; when dry they are removed from the stove, and the barytes is ground up in mills to a fine powder, and then packed for sale.

"Floated barytes" is, or should be, a fine quality prepared by a process of levigation ; in other respects it does not differ from ordinary barytes.

PROPERTIES AND COMPOSITION OF BARYTES.

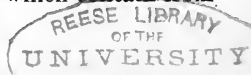
Barytes is a fine and rather heavy white powder, having a specific gravity of 4.5 to 4.75. It has a more or less crystalline structure, which causes it to have a slight gritty feel, no matter how fine it may be ground. It is quite insoluble in all acids and alkalis, a property, or rather properties, which distinguishes it from other white pigments. It is quite unaffected by any injurious influences, such as affect white lead, and, therefore, as a pigment it is the most permanent white known ; for this reason it has been called, and sold, as constant white, permanent white, &c.

In body or covering power it is much inferior to either white lead or china clay, but it is better than zinc white. It mixes very well with oil, of which it takes about 7 per cent. to grind into a stiff paste ; as an oil paint it is satisfactory in use, but for water colours it is not so good, seeming to lose some of its body on mixing with water.

Barytes consists essentially of barium sulphate, $BaSO_4$, but commercial barytes generally contains traces of oxide of iron, silica, &c. The following analyses will show the general composition of barytes :—

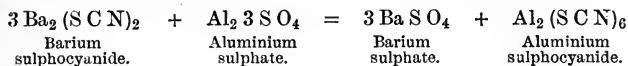
	1.	2.	3.
Barium sulphate, $BaSO_4$, . . .	98.530	99.860	99.68 per cent.
Iron oxide, Fe_2O_3 ,	0.005	0.002	0.01 ..
Silica, SiO_2 ,	0.500	0.040	0.31 ..
Alumina, Al_2O_3 , &c.,	0.965	0.980

It is largely used for mixing with other pigments, especially with white lead, many commercial samples of which contain from



20 to 25 per cent. of barytes; its presence in such is easily detected by its insolubility in acids and its tinging the Bunsen flame green.

Blanc fixe or **artificial barytes** is obtained as a fine white precipitate when sulphuric acid or a sulphate is added to a solution of a barium salt, as, for example, the sulphocyanide with aluminium sulphate; the reaction is shown in the equation—



The sulphate precipitated is allowed to settle, the aqueous layer is run off, fresh water run in to wash the precipitate free from acid, &c., and the precipitate collected on filters. It now forms a pasty mass containing from 70 to 75 per cent. of barium sulphate, and from 25 to 30 per cent. of water, and in this form is largely sold to paper stainers, cotton finishers, and others. It is rarely dried for use as a pigment in oil and water-colour painting. It is much more expensive than ordinary barytes, because the natural barytes is the source from which all other barium salts are derived, and the cost of making first the chloride and then the sulphate from this adds to the cost of the latter. Barium salts, such as the acetate, sulphocyanide, &c., are used in the preparation of mordants, such as acetate of chrome, sulphocyanide of alumina, &c., by double decomposition with sulphates of chrome and alumina, in which case barium sulphate is also formed as a bye-product; this may be used as blanc fixe, provided it is well washed.

ASSAY AND ANALYSIS OF BARYTES.

Barytes should be assayed for colour and covering power in the usual way. There being no cheaper pigment, barytes is never adulterated, but it is used as an adulterant in other pigments. It is distinguished by its high specific gravity, being heavier than any other white pigment except white lead; and by its insolubility in acids, which distinguishes it from all other white pigments except china clay. Barytes can be detected by moistening a little with hydrochloric acid, and holding it on a platinum wire in the lower part of a Bunsen flame, when, if barytes is present, the latter will become tinted with a pale yellow green colour. It is not always easy to see this colour, as sometimes it only comes in flashes, while at others it is more persistent; much depends upon the amount of acid used. With

a little care the presence of barytes in any pigment may be detected by this test.

GYPSUM, TERRA ALBA, MINERAL WHITE.

Gypsum is a mineral found in great abundance in many parts of the world. In this country it is found at Chellaston, near Derby, Aston-on-Trent, and a few other places in Derbyshire, at Newark-on-Trent in Nottinghamshire, Fauld in Staffordshire, and at Netherfield in Sussex. At these places it occurs in large quantities. In smaller quantities it is found in other places. In France there are large deposits, more especially in the district round Paris; it is also found in Germany, America, Canada, and other countries.

Gypsum is the sulphate of calcium, CaSO_4 ; but, unlike the corresponding barium sulphate, gypsum contains 2 molecules of water of crystallisation, so that it has the formula, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; this water of crystallisation confers on it some important properties which will be briefly noticed presently. The composition of gypsum is—

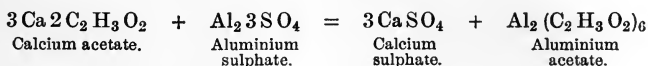
Sulphuric anhydride, SO_3 ,	46·51 per cent.
Calcium oxide, CaO ,	32·56 ,,
Water, H_2O ,	20·93 ,,

Gypsum is found in several forms. The most useful form is that in large amorphous, crystalline masses of a white or nearly white colour and more or less opaque; this is the variety used for a pigment. Often it occurs more or less coloured in a variegated manner; this variety is known as alabaster, Derbyshire spar, and is used for making ornaments. Satin spar is a variety of gypsum occurring in large fibrous silky-looking pieces; this variety is also used as a pigment. Selenite is a variety which occurs in large transparent flat pieces, which have the property of cleavage very highly developed; this is chiefly used for optical purposes. In all its forms gypsum is a soft mineral, easily scratched with the finger nail and easily ground into a white powder. Its specific gravity varies from 2·28 to 2·33.

For use as a pigment gypsum is ground up in the same way as barytes, when it is obtained in the form of a soft white powder of a very good colour known as terra alba, mineral white, satin white, &c.

It can also be prepared artificially. It is a bye-product in some operations, as in preparing acetate of alumina from sulphate of alumina and acetate of lime, or, generally, whenever

acetate of lime or other soluble calcium salts are precipitated by sulphates—



In preparing many coal-tar colours gypsum is obtained, and this bye-product could be used in preparing the so-called aniline lakes (see Chapter IX.).

The colour of gypsum is generally very good and in tone is a bluish-white, rather bluer than barytes, but not so blue as white lead; occasionally samples may have a yellow tint, which is due to the presence of oxide of iron, which, however, can be eliminated by treatment with acids, as in the case of bleaching barytes. It is much lighter than either white lead or barytes, but is rather heavier than china clay or zinc white. Its body is not as good as that of white lead, but it is at least equal to barytes in this respect and is superior to zinc white. It mixes well with either water or oil, and, being neutral in its properties, it can be mixed with all other pigments without affecting them, or being affected by them in any way. On exposure to light and air it is unaffected, being one of the most permanent pigments known. It is used very largely by paper stainers and makers of paper hangings, who prefer it to barytes on account of its having more body when used for that class of work. It is used in the finishing of cotton goods, in paper making, and for a variety of other purposes where a cheap white pigment is required.

Gypsum is slightly soluble in water, about 1 part in 500; this solution will give a precipitate of calcium oxalate on addition of ammonium oxalate and a precipitate of barium sulphate on addition of barium chloride. It is more soluble in hydrochloric acid; long boiling with dilute hydrochloric acid will dissolve it without effervescence, and the solution will show the presence of both calcium and sulphuric acid on the application of the usual tests for those bodies. Gypsum is also soluble in solutions of ammonium salts.

At a temperature of about 300° F. gypsum loses its water of crystallisation and forms a white powder, which has the property of combining with water and setting into a hard mass; this property is a very important one, the manufacture of the white powder being carried on on a large scale, and the product sold under the name of plaster of Paris for various ornamental and useful purposes.

ASSAY AND ANALYSIS OF GYPSUM.—Gypsum should be assayed in the manner given in Chapter X. for tint, brilliancy, covering power, and other properties appertaining to a pigment. A chemical analysis is rarely required and it can be made in the usual way; oxide of iron, silica, barytes, and whiting being the substances most likely to be added or present in a sample of gypsum. Generally, the gypsum offered commercially is nearly pure, containing about 78·5 per cent. of calcium sulphate, the rest being water of crystallisation.

STRONTIAN WHITE.

Strontian White.—Sulphate of strontium, Sr S O_4 , occurs naturally as the mineral celestine in small quantities in many places; it is used on a limited scale as a pigment, being prepared for this purpose in the same way as barytes is made, for which it is often sent out as a substitute. It can also be made by adding a solution of sulphuric acid or a sulphate to a solution of a strontium salt. Prepared in this way it enters into the composition of some patent white pigments.

As a pigment it is quite equal, if not superior, to barytes in some points, and in all respects its properties are identical. If it could be obtained in larger quantities it would be a formidable rival to both barytes and gypsum.

Strontium sulphate may be distinguished from barytes by its lower specific gravity and by its giving a crimson colour to the Bunsen flame; this latter test will also distinguish it from gypsum, from which it is also distinguished by its less solubility in water and acid and its higher specific gravity.

WHITING, PARIS WHITE, SPANISH WHITE, ENGLISH WHITE.

The body sold under all these names, of which the first is by far the most common, is the carbonate of calcium, Ca C O_3 . This compound is one of the most important and abundant of rock-formers; it occurs in large masses, forming, in many cases, mountain ranges of no mean size, and, in a variety of forms, only surpassed in number by those of quartz. It not only occurs as a rock-former, but it is found as a mineral, that is as a body of definite form and composition, in great abundance and variety of shape. One of the rocks made of calcium carbonate is chalk, which, in this country, is largely developed both north and south of London, especially in the

county of Sussex, the coast line of which is celebrated for its chalk cliffs. It is also found in the north of France, in the district between Paris and the English Channel. In England it is extensively quarried for a variety of purposes, one of which is the manufacture of whiting; and English whiting has a world-wide reputation for quality. Chalk is essentially a rock of organic origin, and it owes its formation to the operations of certain minute organisms known as *Foraminifera*; these bodies have the property of secreting a shell of calcium carbonate, and chalk is the remains of a deposit of the shells which has been formed after the death of the animal that inhabited them. Chalk is very nearly pure calcium carbonate, but it contains traces of silica, oxide of iron, alumina, &c. Besides the traces in which silica is found distributed throughout the main mass of the chalk, it also occurs in large masses of very irregular shapes known as flint.

For use as a pigment, the chalk is quarried, ground under water in edge-runner mills to a coarse powder, then passed to flatstone mills, where it is ground very fine; from which mills it is run into tanks, in which the coarser and heavier grit and sand settles, while the finer chalk passes on to other tanks in which it settles. When the settling tanks or pits are full, the chalk or whiting is dug out and dried. It is first taken to a hot room, on the floor of which it is thrown in heaps. Under the floor are a number of flues connected with a furnace fed from the outside of the chamber; sometimes the flues do not pass under the floor of the chamber, but round three sides of it, much in the same manner as in the drying-room used in making barytes. In this room it remains about twelve hours, when the great bulk of the water it contains will have evaporated away. The partially dry mass is now cut into masses of a cubical shape, and taken to a large drying-room, constructed similarly to the one described under barytes. In this hot chamber it is placed on iron racks, and kept there until it is thoroughly dry, which will take from 24 to 48 hours, according to the degree of dryness of the whiting, and to the temperature of the drying stove; the drying is also facilitated if a current of air is sent through the drying-room during the process, as is done in some works. The temperature of the drying stove should not be too high, and in arranging the whiting on the racks it is advisable not to place it in any position where it is liable to be subjected to extreme heat. After being dried, the whiting is ground in a flatstone mill before it is sent out for use.

It may be stated that one reason for avoiding over-heating

during the process of drying is to prevent the conversion of the carbonate of lime into quicklime. One of the properties of carbonate of lime is that when heated it loses its carbonic acid, and passes into the state of oxide, which has some powerful alkaline properties undesirable for some purposes to which whitening is put.

Paris white is a finer quality of whitening, prepared from chalk in the same way, but the grinding is more thoroughly done. Spanish white is an old name given to Paris white sold in a cylindrical form, prepared by moulding the wet material into that form, and allowing it to dry in the open air.

COMPOSITION AND PROPERTIES OF WHITING.—

Whiting is a dull white powder of an amorphous character, and soft to the feel; it is moderately heavy, the specific gravity being about 2.5 to 2.8. It consists chiefly of calcium carbonate, but it may also contain traces of silica, water, &c. The following analysis of an ordinary commercial sample will show the average composition of whitening:—

Calcium carbonate, CaCO_3 ,	94.795 per cent.
Silica, SiO_2 ,	3.030 "
Water, H_2O ,	2.175 "

It is quite insoluble in pure water, but in water containing carbonic acid gas in solution it is soluble. It is also soluble in acids such as acetic, hydrochloric, nitric, &c., with effervescence due to the evolution of carbonic acid gas. Sulphuric acid decomposes it with effervescence, carbonic acid being evolved, and insoluble calcium sulphate formed. There are but few white pigments which are soluble in acids with effervescence; white lead and whitening are the most common, while the carbonates of barium, strontium, and magnesium are occasionally met with.

Heat decomposes it with the evolution of carbonic acid gas, CO_2 , and the separation of calcium oxide, quicklime, CaO ; this property is taken advantage of in preparing lime for making cements, mortars, &c.

As a pigment it is mostly used as a body colour in distemper work, colouring walls, ceilings, &c., using water as a vehicle. It is not used as an oil colour, for it is subject to the defect that, when mixed with oil, it loses its white colour and turns a dirty grey; mixed with about 18 per cent. of linseed oil, it forms the useful article known as putty.

It has a tendency to be somewhat alkaline in its properties. In this respect much depends upon the care which has been exercised in drying the whitening during the process of manufac-

ture; over-heating is apt to cause the formation of small quantities of quicklime, which increases the alkaline properties of the whiting. It is not safe, therefore, to mix it with such pigments as Prussian blue, chrome yellow, verdigris, emerald green, &c., which are more or less affected by alkalis. Most other pigments—ultramarine, yellow ochre, oxide reds, &c., are not affected by whiting in any way.

It is quite permanent when used as a pigment, and is not at all acted on by any of the ordinary atmospheric agents which are often destructive to pigments.

ASSAY AND ANALYSIS OF WHITING.—The assay and analysis of whiting is a matter which is rarely required, the pigment is so cheap that it is not subject to any adulteration. When, however, an assay is required, it can be done in the usual way.

Whiting is distinguished by the following tests:—It is soluble in dilute hydrochloric acid with much effervescence; there may be left undissolved small traces of silica in a gelatinous form, but no considerable amount of white powdery insoluble residue will be found. On adding to this solution ammonium chloride and ammonia, no precipitate of iron or alumina should be obtained, or, at most, a very slight one. On further adding ammonium sulphide, no precipitate should be obtained. Addition of ammonium oxalate to the same solution throws down a white precipitate of calcium oxalate. The filtrate from this should not give with sodium phosphate more than a mere trace of a precipitate of magnesium phosphate.

The quantity of calcium carbonate or whiting which may have been added to any pigment may be ascertained by throwing it down as calcium oxalate, as described above, and then filtering off this precipitate; but it is best to allow it to stand for some time before filtering, so as to give time for the precipitation to become complete. The precipitate is well washed, then dried, placed in a weighed crucible, burned, and weighed in the usual manner. The weight of the residual calcium carbonate gives the weight of the whiting in the sample taken.

MAGNESITE

is the form in which magnesium carbonate, $MgCO_3$, occurs in many localities, closely resembling the more crystalline varieties of calcium carbonate in appearance. Ground up and levigated with water it has been offered, from time to time, as a pigment, but it has not come into general use. It is rather heavier than

whiting, its specific gravity being about 3.05. Its colour is good, and it forms a dense white powder; in body and covering power it is quite equal to barytes. It works well in both oil and water, and mixes fairly well with other pigments, although it has a slight tendency to possess alkaline properties. It is quite permanent, and resists exposure to light and air.

Magnesite may be distinguished by the following tests:— It is soluble in dilute hydrochloric acid, or in sulphuric acid with effervescence. This solution gives no precipitate with ammonium chloride and ammonia, ammonium sulphide or ammonium oxalate, but gives a copious white, somewhat crystalline, precipitate of ammonium magnesium phosphate on addition of sodium phosphate to an ammoniacal solution; this precipitate, on ignition, is converted into magnesium pyrophosphate.

CHINA CLAY.

China clay or, as it is sometimes called, kaolin, which is its Chinese name, is a natural product, and only requires levigating and drying to prepare it for use as a pigment. It owes its name to its use in the manufacture of the white and finer varieties of pottery. Prior to its discovery in this country the pottery in common use had a brown colour, due to the use of clays highly contaminated with iron, and much of the best kinds of white pottery were imported from China; hence the use of the term, "china," for white pottery. When the existence of the deposits of china clay in Cornwall was found out, and its use in making pottery became general, the goods so made were denominated "china," and the material "china clay." As a pigment it is not used to the extent its many good qualities entitle it to.

ORIGIN AND COMPOSITION OF CHINA CLAY.—

In England and other countries where china clay is found it is invariably associated with granite rocks, and is evidently a decomposition product from them. The exact cause which has led to the decomposition of the granite rocks in those places where china clay is found, and to its not undergoing this decomposition in others, where it is equally well developed, is a matter which at the present moment is one of uncertainty.

Granitic rocks are formed by the aggregation of three minerals in various proportions; these three minerals are quartz, felspar, and mica. Quartz is the special form of silica (oxide of silicon, Si O_2) which occurs in these granitic rocks; it is absolutely unchangeable by any amount of exposure to the atmosphere.

In granites it forms the base mass throughout which the other minerals are distributed.

Mica is a double silicate of potassium and alumina, having usually the composition shown in the following analysis :—

Silica, Si O_2 ,	46·3 per cent.
Alumina, $\text{Al}_2 \text{O}_3$,	36·8 „
Potash, $\text{K}_2 \text{O}$,	13·7 „

but the proportions vary in micas from different districts ; in some varieties of mica the potash is replaced by magnesium, in others by sodium. Mica is characterised by crystallising in thin transparent flakes or plates, which are sometimes found of large size ; these flakes have the property of cleavage very highly developed, so that mica can be easily split up into very thin leaves. It is a very refractory substance, and will resist a considerable amount of exposure to atmospheric influences without being decomposed ; it will resist heat to a great extent. During the natural decomposition of the granitic rocks, which gives rise to the formation of china clay, the mica and quartz undergo no change whatever.

The third mineral which is found in granite is felspar ; this occurs in the rock in the form of white or slightly reddish, opaque rhombic crystals. In some granites the crystalline form of the felspar is well developed, while in others it assumes an amorphous appearance. There are many varieties of felspar, but they are all of them double silicates of alumina and of the alkali-metals, while in some calcium replaces to a greater or less extent the alkali-metal. The most important and most common felspar is the potash variety, known as orthoclase ; this has the composition shown in the following analysis :—

Silica, Si O_2 ,	64·20 per cent.
Alumina, $\text{Al}_2 \text{O}_3$,	18·45 „
Potash, $\text{K}_2 \text{O}$,	17·35 „

On comparing this analysis with that of the mica given above it will be seen that the felspars contain a larger proportion of silica and of the alkaline constituent, while the proportion of alumina is only about one-half that found in the micas.

The formula of felspar is $6 \text{ Si O}_2, \text{ Al}_2 \text{ O}_3, \text{ K}_2 \text{ O}$.

The soda-felspar has a similar composition ; in some felspars both alkali-metals are present.

Felspar is capable of undergoing decomposition when exposed to the destructive action of the atmosphere, which decomposition is probably chiefly brought about by the action of the carbonic

acid and water which are always present in the atmosphere; probably the alkali is eliminated in the form of carbonate, which, being soluble in water, passes into solution in the springs which rise in the granite, while the silica and alumina are left behind in an insoluble form, the kaolin or china clay of the potter. The average composition of china clay is :—

Silica, Si O_2 ,	47 per cent.
Alumina, $\text{Al}_2 \text{O}_3$,	40 "
Water, $\text{H}_2 \text{O}$,	13 "

which corresponds to the formula, $2 \text{Si O}_2, \text{Al}_2 \text{O}_3, 2 \text{H}_2 \text{O}$. But, as a rule, the composition of the china clay found in various localities varies somewhat from this, as will be seen in the following analyses of some china clays from several widely-separated localities, which are quoted from several sources.

ANALYSES OF CHINA CLAYS.

CONSTITUENT.	Cornwall.	China.	Laurence Co., America.	French.	Dartmoor.	Cornwall.
Silica, Si O_2 ,	46·78	50·50	47·13	48·37	47·20	46·32
Alumina, $\text{Al}_2 \text{O}_3$,	39·60	33·76	36·76	34·95	38·80	39·72
Water, $\text{H}_2 \text{O}$,	13·16	11·22	15·13	12·62	12·00	12·67
Potash, $\text{K}_2 \text{O}$,	0·12	1·90	...	2·4	1·76	0·44
Ferric oxide, $\text{Fe}_2 \text{O}_3$,	0·09	1·80	trace.	1·26	...	0·27
Lime, Ca O ,	0·07	...	0·04	...	0·24	0·36
Magnesia, Mg O ,	0·80	0·36

China clay occurs in large deposits along with the other constituents of undecomposed granite, the china clay usually forming from 15 to 20 per cent. of the whole deposit. The deposit does not usually occur in layers, but in basins in the surrounding granite; over the deposit there is usually a layer of soil known locally as the "overburden," which varies in thickness from one to several feet. Fig. 11 is a drawing of a china-clay deposit taken from Mr. David Cook's *Treatise on China Clay*. The deposits of china clay are often of great depth.

MANUFACTURE OF CHINA CLAY.—The process of extracting the china clay from the undecomposed quartz and mica is essentially one of levigation and is comparatively simple.

When a deposit of china clay has been found, the overburden is removed and usually two shafts are sunk ; one of these is as close as possible to the edge of the deposit and is known as the permanent shaft, the other is sunk in the centre of the deposit and is known as the "rise," partly because it is often not sunk from the top ; but the permanent shaft is first sunk and then a

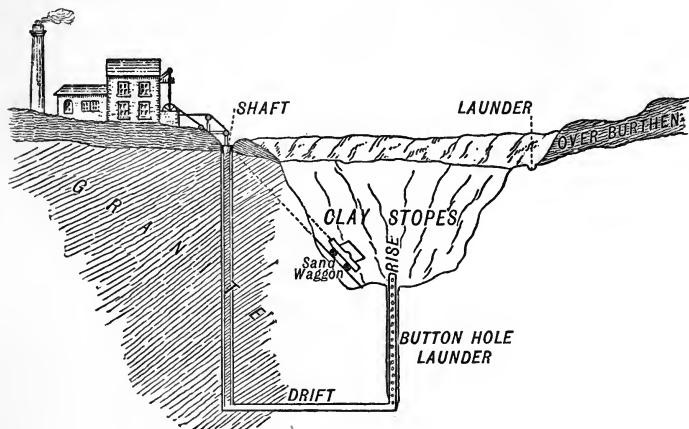


Fig. 11.—China-clay works.

drift is dug to the centre of the deposit and the centre shaft dug out from the bottom ; in any case, whether the rise is sunk from above or dug out from below, a drift or horizontal shaft connects it with the permanent shaft. The size of these shafts varies in different places, but it is not necessary that they should be of large dimensions ; the rise in particular need not be any larger than can comfortably be excavated.

The permanent shaft is fitted with pumps, the use of which will be seen presently.

The rise is fitted with a square wooden pipe of 9-inch side and long enough to reach from the top of the rise to the horizontal drift at the bottom. In one side of this tube is a number of holes about 4 inches in diameter and at a distance of 1 foot from centre to centre ; before placing in position these holes are stopped up by plugs known as "buttons," and the tube itself is known as the "button-hole launder"—"launder" being a local term to signify any tube or trough through which liquors or materials can flow. After the button-hole launder is placed

in position in the rise all the space between it and the sides of the rise is filled up with clay pressed down rather tightly.

One essential feature of china-clay works must be a plentiful supply of water; without this it cannot be profitably carried on, and the source of supply should be, if possible, above the works, so that it may be supplied to any part by the aid of gravity alone; if it be on a level or below the works, then pumping becomes a necessity, and this should be avoided whenever possible, as it is a source of expense which reduces the profit of working the deposit.

A china-clay works is shown in Fig. 11, in which the relative position of the clay deposit with the surrounding rocks is shown, with the overburden, the permanent shaft, the button-hole launder, and the pumping house.

The deposit of china clay is worked in the following manner:—The overburden is removed and then a current of water is directed against the sides, known at the works as the “stopes” of the deposit; naturally these currents of water will wash the china clay, &c., to the lowest part, which is the centre of the deposit. At the bottom of the stopes is arranged a hollow or sand pit; in this the sand or quartz collects, and is removed from time to time by means of a sand waggon which is hauled up the sides of the clay pit on an inclined tramway by means of a windlass driven by the engine. The clay along with the mica flows through the topmost hole in the button-hole launder into the horizontal drift at the bottom, from thence it passes into the permanent shaft, from which it is again pumped to the surface to be treated in the manner presently to be described. As the level of the china-clay deposit descends, the buttons in the launder are removed until, finally, when all the clay is worked out, the bottom of the deposit is reached, and with it the last hole in the launder. The length of time required to work out a deposit depends entirely on its extent, which may be small or large; the deposits, as a rule, are large and take some years to work out.

The crude clay as it comes from the pits or stopes is still impure; it contains much fine sand or quartz, most of the mica (which does not separate so readily out of the clay as the sand does), together with undecomposed particles of felspar; from these it requires to be separated; this is done by a process of levigation by means of water. In early times when the clay was first worked this was done in a crude form, usually in a series of tubs, but now a better system is adopted, which is shown in Fig. 12.

From the button-hole launder the water containing the clay,

sand, mica, &c., is pumped into a series of troughs of wood, generally known as "launders;" these are long and wide; across these at intervals are placed a number of pieces of wood, called the "drags," which serve to impede the flow of the water, and cause it to form a series of pools, in which the heavier particles of sand can collect. These launders are emptied of the sand which accumulates in them from time to time, so as to give

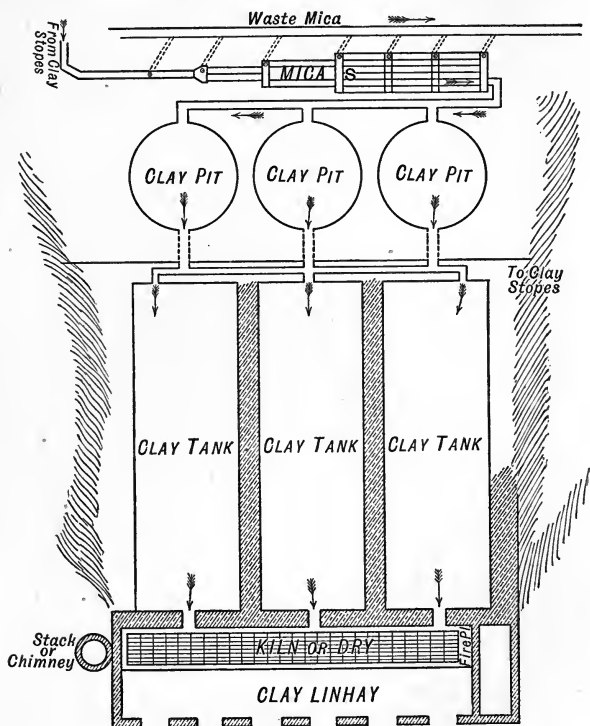


Fig. 12.—China-clay works.

plenty of room for the sand to deposit. From the launders the water, with the clay and mica, passes on to what are called the "micas," an ingenious arrangement for promoting the deposition of the light and flaky pieces of mica. The micas are a series of troughs 20 feet long, 2 feet wide, and 6 inches deep, placed side by side in a peculiar manner. The clayey water from the launders

first passes into two of these, then from these into three, then again into four, and, finally, into six of these mica troughs; thus as it passes to the exit end the flow of water is spread over a larger surface, and becomes more feeble, a condition which facilitates the deposition of the mica. The micas get filled in about eight hours, when they are flushed of their contents with water, which carries the deposited mica through suitable channels into the waste mica pits.

Next in order to the micas is a set of settling pits. These are usually three in number, sometimes more, according to the quantity of clay which is being worked. These pits may be of any shape, but, as a rule, they are made circular (or rather cylindrical) in form, 7 feet in diameter, and 40 feet deep. Into one of these pits the clayey water from the micas is run until it is full, when the current is changed and the water run into the second one until it is full. While the filling of the second pit is proceeding, the clay in the first one is settling, and, probably, by the time that the second is quite full, has completely settled. The current of clayey water from the micas is now diverted into the third pit, while the clay in the second one is settling. The water in the first pit is now run or pumped off, and is generally used over again for washing the clay from the stopes. From a pit full of clayey water there will usually be obtained a deposit of clay about 5 feet in depth, which still contains a large proportion of water; in such a thickness of clay, and 7 feet in diameter, there will be something like 285 tons of dry clay. The clay in the first pit is dug out and thrown into what are called clay tanks, where a further settling takes place; when all the clay has been dug out the pit is ready to be filled again with water from the micas. This alternation of filling, settling, and emptying is carried out with the three pits in succession, so that it will be seen that for continuous working a series of not less than three pits is required; if more pits are used, then the time of settling can be lengthened, which would have the advantage of giving a drier clay and shortening the subsequent operations.

From the settling pits the still wet clay passes to the settling or clay tanks; these are, at least, three in number, corresponding with the three settling pits; in some works there are more; much, of course, depends upon the quantity of clay it is desired to turn out. These settling tanks are usually rectangular in shape, about 60 feet long by 7 feet wide and 6 feet deep, and they will hold about 1000 tons of clay; in these tanks settling occurs, and the clay begins to assume the consistency of lard; when this happens no more clay is sent into it from the pits, and the clay in the

tank is allowed to settle. The water is then run off, and the clay transferred to the drying place, where it is dried ready for sale.

The clay in the clay tanks contains about 50 per cent. of water, most of which must be driven off before the clay is marketable. This drying operation is done on a series of flues, technically known as the "dry;" a usual size is 60 feet long by $13\frac{1}{2}$ feet wide. In this kiln or dry there will be three fireplaces, two at one end, and one at the other, each fireplace having three flues about 9 inches wide; the sides are formed of brickwork, but the bottom is usually made of sand, partly because sand is a bad conductor of heat, and partly because any water which may drain through from the top of the flue readily sinks into it and drains away. The tops of the flues forming the bed of the dry is made of fireclay bricks about 18 inches wide. On these fireclay bricks the wet clay from the tanks is thrown, and it remains until it is dry. It takes about 1 ton of coal to dry 10 tons of clay.

After being dried on the dry the clay is thrown on the floor of the clay linhay, which is a storage place for the dry clay, from whence it is sent out as required.

The dry and the linhay are parts of one large room, being covered over with a roof, as is seen in the drawing (Fig. 12).

COMPOSITION AND PROPERTIES OF CHINA CLAY.—China clay is essentially a hydrated silicate of alumina, as has been already stated; but there are some minor differences in the composition of samples from various localities, as will be seen on examining the table given on p. 81; these are, of course, primarily due to differences in the composition of the granite from which the china clay has been formed, and, secondarily, to the degree with which the decomposition has proceeded.

China clay, or kaolin, is a fine, white, amorphous powder having slight adhesive properties and adhering to the fingers when moist.

It is light, its specific gravity being about 2.2; so that it is the lightest of all the white pigments. The best qualities have a very soft unctuous feel; the common qualities are rather rougher, but none have the slightest trace of grittiness about them. The best qualities have a pure white tint, others a more or less yellowish tint, which the china-clay makers are accustomed to disguise by adding a small quantity of ultramarine.

It is quite insoluble in water, dilute acids, and alkalis. Boiling in strong sulphuric acid for some time decomposes it

with the formation of a gelatinous residue of silica and a solution of alumina sulphate. Hydrochloric acid has little action on it.

As a pigment it is quite permanent, resisting perfectly exposure to the atmosphere and to light for any length of time. As a pigment it is not, however, much used. In oil it loses its body and becomes more or less transparent. It can be used in water-colours and in distemper work with good results, and it is used in paper-making and paper-staining. It also finds a use in the preparation of the aniline lakes, especially when these are to be used in paper-staining.

Its principal uses are for making pottery, ultramarine, finishing cotton cloths, making paper, &c.

ASSAY AND ANALYSIS OF CHINA CLAY.—China clay can be assayed for colour or tint, covering power, &c., by the methods given below. An analysis is rarely wanted, since it is never adulterated, while for all pigment purposes absolute chemical purity is not required.

WILKINSON'S WHITE LEAD AND PATTINSON'S WHITE LEAD are oxychlorides of lead prepared in various ways; neither pigment is now used.

Wilkinson's white was patented in 1799, and is made by digesting litharge with a solution of salt until it acquires a pure white colour. Unfortunately, as it is the product of various operations, there is a lack of uniformity in its composition, which is much against its use as a commercial article. Another method of making it is to precipitate acetate of lead with hydrochloric acid, and to digest the precipitate of lead chloride obtained with basic lead acetate.

Pattinson's lead was made by treating chloride of lead with lime, when it forms the basic chloride, a white insoluble body having a fair body, but wanting in uniformity of composition.

CHAPTER III.

RED PIGMENTS.

THIS is a fairly numerous and important class of painters' colours. They are derived from both inorganic and organic sources, and include some of the most highly valued and most used of the pigments at the disposal of the painter and artist.

VERMILION.

Vermilion has been used for a long time as a pigment. It is a compound of mercury and sulphur in the proportion of 200 parts of the former to 32 of the latter; its chemical name is mercuric sulphide, and it has the formula, HgS . It is found naturally in large quantities as the mineral cinnabar, especially in Spain; but it rarely occurs naturally of sufficient brightness to be used as a pigment, and is, therefore, mostly made artificially. When a current of sulphuretted hydrogen is passed through a solution of a mercuric salt a black precipitate of the mercuric sulphide, identical in composition with vermilion, is obtained; this precipitate is characterised by being insoluble in most single acids, but soluble in a mixture of hydrochloric and nitric acids. By heat it is volatilised, and the sulphide sublimes in the form of a red powder; this transformation from black to red can also be brought about by boiling it for some time with aqueous solutions of the caustic alkalis or of alkaline sulphides. What the cause of the change may be is rather uncertain; probably there has been a re-arrangement of the atoms in the molecule of mercuric sulphide; there are many cases known of similar differences in the colour of inorganic compounds, as, for example, cadmium sulphide and basic chromate of lead. Although it is generally considered that the molecule of each of these poly-coloured bodies is always made up of the same number of atoms, yet there is no direct evidence on that point; and it is quite possible that in the different modifications of these bodies the number of atoms may vary and, therefore, be arranged dif-

ferently. This subject requires further investigation before the point can be definitely decided.

MANUFACTURE OF VERMILION.—Vermilion can be made both by dry and wet methods; the former are those mostly used as they give the best product; the latter are employed in some places but not to the extent of the dry methods. The product is not quite equal, although very little inferior to that made by the dry methods. The Chinese have long been renowned as makers of vermilion; their product is finer and more brilliant in tone than that made in Europe. Until lately, the process by which Chinese vermilion was made was not known with certainty, although it was conjectured that the wet method was used, and, consequently, this method is usually described in text-books as "The Chinese method;" but this is now known to be erroneous, and that Chinese vermilion is made by a process very little different from that used in Europe. The difference in quality almost entirely arises from the greater care the Chinaman takes in making it.

DRY METHODS—1st. **Dutch Process.**—This is the method commonly used for making vermilion. It is conducted in two stages. In the *first stage* 108 lbs. of mercury are mixed with 15 lbs. of sulphur in a shallow iron pot; this is usually placed over a furnace so that a gentle heat may be applied; the two bodies gradually combine together to form a black sulphide of mercury or "ethiops" as it is called, the union being promoted by a continual stirring with an iron spatula. When the combination is considered by the workman to be complete, the iron pot is emptied of its contents into a store pot and a fresh mixing is made. The "ethiops" contains some free mercury, free sulphur, as well as sulphide; the proportions will vary according to the length of time the operation has been continued, the heat applied, &c.

The *second stage* consists in heating black ethiops in a suitable furnace, whereby it is converted into the red vermilion. A number of simple furnaces or fireplaces are built side by side to form a range; in each of these fireplaces is placed a cylindrical earthenware pot, so arranged that the lower two-thirds of the pot are in, while the upper third is outside the furnace. The pots are fitted with a closely-fitting iron lid, in the centre of which is a small charging hole. The fire in the fireplace is lighted, and, when the pot has been heated to a red heat, a small quantity of the black ethiops obtained in the first stage is charged into the pot; much of the sulphur in the ethiops burns off; when there is no further appearance of sulphur fumes

from the pot more ethiops is added; these additions are continued at intervals for thirty-six hours, the cover being kept on during the whole of the operation; then the pots are allowed to cool down; when cold the cover is removed and the vermilion is found as a crust on the under side of the cover and around the sides of the upper portion of the pot. This crust is carefully removed, the red portions being placed on one side for further treatment, while any black, unchanged portions are mixed with some fresh ethiops to be again heated. The red vermilion is now ground up as fine as possible with water; if not of sufficiently brilliant colour it may be treated either with acids or alkalies as is described below, well washed with water, allowed to settle out of the wash waters, dried at a gentle heat and sent into the market ready for use.

2nd. Chinese Method.—A few years ago a description* of the process used by the Chinese for the preparation of vermilion appeared in several journals, and at the Colonial and Indian Exhibition held in 1886 there was shown in the Hong Kong Court a Model of a Chinese vermilion factory. Like the Dutch method, the Chinese process is in two stages, and is carried out as follows:—

An iron pan, measuring 25 inches in diameter and 6 inches deep, is placed over a charcoal fire; into this pan is placed $17\frac{1}{3}$ lbs. of sulphur and $37\frac{1}{2}$ lbs. of mercury; heat is applied, and the mixture stirred until the materials melt and become amalgamated together; then $37\frac{1}{2}$ lbs. more mercury are added, and the heating and stirring continued until the two bodies have become united. The pot is now removed from the fire and water added in sufficient quantity to form a paste, which has a blood-red colour; the *first stage* of the process is now complete.

Second Stage.—The crude vermilion obtained in the first stage is broken up into small pieces and placed in iron pans measuring $29\frac{1}{4}$ inches in diameter and $8\frac{7}{8}$ inches deep; on the top of the vermilion is placed a number of broken pieces of porcelain plates arranged in the form of a dome; over all is placed the pan used in the first stage, the two pans being luted together with clay, and a few vent holes left in the luting. The pans are placed on a furnace, which is constructed in a simple manner; usually a number are built side by side. The pans are heated for 18 hours at a dull red heat, after which they are allowed to cool down; when cold, the pans are opened, when

* *Oil and Colourman's Journal*, 1883, p. 86. *Chemical News*, 1884, vol. 50, p. 77.

the vermilion is found as a red sublimate on the under side of the porcelain plates and the upper pan; this red mass is collected and transferred to another place for the finishing operation. The crude vermilion which has been scraped off the porcelain plates is now ground as finely as possible with water in a mortar; the ground colour is next mixed with water in which alum and glue in the proportions of 1 oz. of each in a gallon of water have been dissolved, and allowed to stand for a day; it settles down and is found as a cake at the bottom of the vessel, which is made of earthenware, and has a capacity of 6 gallons. The top of the cake is of fine quality; this is separated from the bottom portion, which is re-ground up with the next batch; sometimes the top portion is re-ground. After being washed well with clean water, the finely-ground vermilion is dried and then packed up ready for sale.

WET METHODS—1st. Common Method.—In making vermilion by this method 68 lbs. of sulphur and 300 lbs. of mercury are mixed and ground together until they are thoroughly incorporated; they are then added to a solution of 160 lbs. of caustic potash in water, placed in iron pots and heated to a temperature of 45° C., which is maintained for some hours. For the first two hours the water lost by evaporation is made good, but after this no further addition is made, and the mass is kept constantly stirred. After some time the mass, which has at first a blackish appearance, turns brown and then gradually passes into red; when it is considered that the colour is fully developed the mixture is removed from the fire, well washed in water and dried. This process requires careful watching.

2nd. Firmenich Process.—The process described by Firmenich* consists in taking 10 parts of mercury and agitating them with 2 parts of sulphur and 4½ parts of potassium pentasulphide (prepared by heating potassium sulphate with charcoal) and boiling the residue with excess of sulphur for three to four hours, when it takes a brown colour; it is then kept at a temperature of 45° to 50° C. for three to four days, being agitated at intervals during that period; it is next treated with water, then with a weak lye of caustic soda (to free it from excess of sulphur), washed thoroughly and dried.

In these wet processes it is important that care be taken not to heat the mixtures of mercury, sulphur, and alkali to too high a temperature; from 45° to 50° C. is high enough. Time, not

* *Chemical News*, vol. v., 1862, p. 247.

heat, seems to be the most important element to consider in these processes ; too great a heat turns the vermilion brownish.

The brilliancy or fire, as it is sometimes called, of the vermilion may be increased during manufacture by

1st, Grinding very fine and levigating ;

2nd, By warming with a caustic soda lye ;

3rd, By treatment with nitric acid ;

4th, By treatment at about 50° C. with a mixture of the caustic and sulphide of potash ; and

5th, By treatment with hydrochloric acid.

Any of these, or a combination of them, may be, and are, used for this purpose.

PROPERTIES OF VERMILION.—Vermilion is a very bright scarlet powder. It is the heaviest pigment known, its specific gravity being 8·2, which causes it to settle readily out of paints, &c., in which it is used, and renders its application somewhat troublesome. It is very opaque, and, consequently, has great covering power or body. It is quite insoluble in water, alkalies, and any single acid, but a mixture of nitric and hydrochloric acids dissolves it with the formation of a colourless solution of mercuric chloride ; as a rule, very few substances are capable of acting on vermilion.

Heated in a tube out of contact with air, vermilion first turns brown, then sublimes in the form of a red sublimate. Heated in contact with air, vermilion burns with a pale blue, lambent flame, giving off vapours of sulphur dioxide and mercury oxide ; if pure, there will be but a trace of ash left ; thus a sample of good vermilion analysed by the author contained

Sulphide of mercury,	99·63
Ash,	·37
	100·00

This forms a reliable test for the adulteration of mercury, for any adulterant which may be used will be left behind on heating. The usual adulterants employed are red lead, oxide of iron, red lakes, vermilionettes, &c. The presence of any of these is easily ascertained by the application of the characteristic tests, which will be found described under each particular pigment.

When used as an oil-colour vermilion is permanent ; when used as a water-colour it is generally considered to be permanent, but the experiments recently made by Capt. Abney and Dr. Russell throw some doubt on this point ; they found that vermilion used as a water-colour turned brown after two years exposure to light

and air, probably owing to an intermolecular change; much appears to depend on the care with which the vermilion has been made.

RED LEAD.

This valuable red pigment has been known and used for a very long time. Pliny, in his writings, describes this body, which in his time was known as minium, under which name it is also frequently referred to in later writings. Pliny also mentions its use for adulterating vermilion. Davy, who had an opportunity of examining the contents of some pots of colour found in the remains of Roman and Greek cities, frequently found red lead among them. How it was made by the ancients is not definitely recorded.

MANUFACTURE OF RED LEAD.—There is only one process for making red lead, which consists of two stages—the

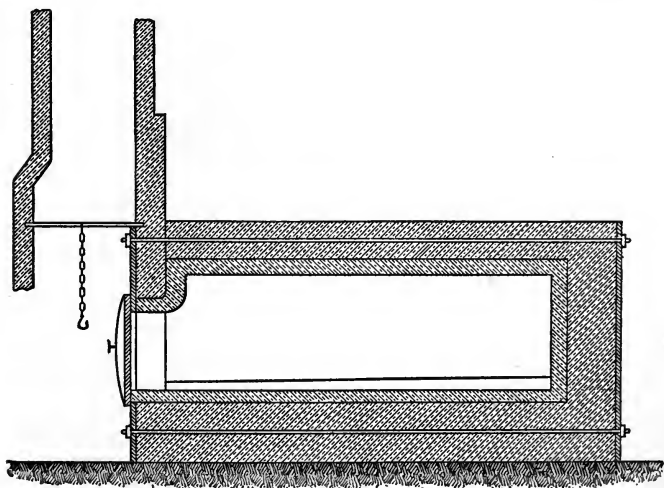


Fig. 13.

first stage has for its object the conversion of metallic lead into monoxide of lead; in the second stage this oxide is converted into red lead.

1st Stage, Drossing.—This is conducted in what is called the “drossing oven,” a kind of reverberatory furnace of which Figs. 13

and 14 show respectively the longitudinal and vertical sections. From these drawings it will be seen that it is a low oven, open only in front, over which is constructed a hood and chimney to carry off the products of combustion, &c., from the furnace. The bed usually measures about 11 feet by 12 feet 4 inches, and is divided (as shown) into three divisions—the central one measures 8 feet 4 inches wide, and constitutes the bed or hearth of the furnace, while the two side divisions measure about 2 feet each, and form the fireplaces of the oven, as a

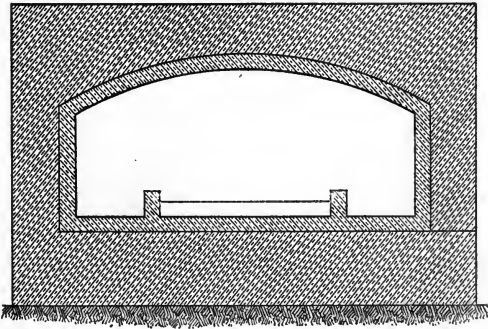


Fig. 14.

rule, they are not fitted with firebars ; the partitions between the fireplaces and hearth are formed of firebrick ; the bed of the furnace is made to slope from the back to the front, usually the back is about 7 inches higher than the front, while it also slopes slightly from the side to the centre. In the front of the furnace are three doors—the two side ones are for feeding the fires, while the centre one serves for introducing and extracting the material, and for working the charge while in the furnace ; it is placed a little higher than the two side doors so that a draught is generated through the latter and out of the centre door ; in the top of this door an opening is left so that the products of combustion, &c., can pass out and up the chimney.

This furnace is open to improvement, and an improved form is shown in Fig. 15, from which it will be seen that this form of furnace has firebars fitted to the fireplaces.

The operation of drossing is carried out in the following manner :—22 cwts. of lead, which is the quantity usually dealt with in one charge, are placed in the furnace, which is now

raised to a dull red heat, just enough to melt the lead, the molten lead being prevented from flowing out of the furnace by the construction of a dam, formed of pieces of dross or "leanings" from previous workings, across the front of the hearth; the melted lead rapidly becomes coated with a layer of

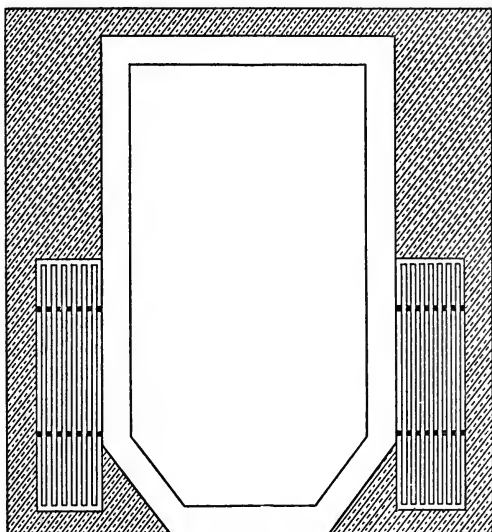


Fig. 15.

oxide, the formation of which is hastened by rabbling the lead and pushing the oxide as it is formed to the back of the furnace, the object being to always have a fresh surface of lead exposed to the oxidising action of the air which passes through the furnace. The workmen by a peculiar splashing action while rabbling expedite this oxidation very much; at intervals pigs of lead are thrown into the furnace. This dressing takes about 10 to 12 hours, at the end of which time the dam across the front of the furnace is broken down, and the unmelted lead allowed to run out, while the "dross" or "casing," as it is called, is taken out to be worked for the next stage. The furnace is now ready for another charge.

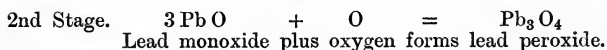
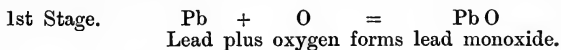
The "dross" or "casing" has a rather bright yellow colour, and is coarse in texture; it consists essentially of the monoxide of lead, PbO , but still contains some unoxidised lead. It is

now ground and levigated with water; the oxide grinds to the form of a fine powder, while the lead is simply flattened out, and by sieving can easily be removed; it is sent back again into the furnace, while the ground oxide is washed by a stream of water into settling tanks, where it settles out in the form of a paste, which is ready for use in the next stage.

One point of importance in the dressing stage is to see that the temperature is carefully regulated, so that, while it is above the melting point of the lead and therefore in a molten state, yet it is below the melting point of the casing; as the margin is not great, considerable care has to be taken to avoid overstepping the limit. If the casing is allowed to melt it passes into litharge and this cannot be converted into red lead. The dross or casing is also known as massicot.

2nd Stage, Colouring.—The next operation consists in heating the dross obtained in the first stage, either in the same oven or in another, which only differs from the dressing oven in a few minor details. The colouring oven is heated to a low red heat, care being taken to ensure a large supply of air. The operation takes about 48 hours, and the mass is frequently rabbled during that period; after it has been in about 12 hours a sample is taken out and its colour examined; this sampling is repeated at the end of each twelfth hour and near the end of the operation more frequently. When the red lead has attained the correct colour, the fires are drawn and the furnace allowed to cool down; when cold, the red lead is drawn from the oven, ground as finely as possible, and sent into the market.

The change which takes place in the transformation of the metallic lead into red lead is shown in the following equations—



Theoretically, 100 lbs. of lead should yield 110.36 lbs. of red lead; practically, about 108 lbs. of red lead are obtained, which is a very near approach to the theoretical amount. The best red lead for painters' use is made from pure lead, as the presence of impurities in the metal has a material and injurious influence on the colour of the product; iron, in particular, causes the colour to be dark. For glass-makers' red lead a pure product is absolutely necessary, as an impure lead causes the glass to be coloured, not white as it should be.

Burton's Process.—Although the only process at present

worked for the preparation of red lead is the one described above, yet in 1862 Burton patented a process for making red lead from sulphate of lead, in which 1 equivalent or 1.894 parts of lead sulphate are mixed with 1 equivalent or 0.665 part of sodium carbonate and 1 equivalent or 0.143 part of sodium nitrate. The mixture is heated to a dull red heat with an excess of nitre; the fused mass is lixiviated with water, whereby the red lead formed is separated from the alkaline salts, and this is washed and dried.

PROPERTIES AND COMPOSITION OF RED LEAD.

—Red lead is a heavy, bright red powder of an orange hue, its specific gravity being 8.53. Heat turns it to a dark brownish-red, but the colour is restored on cooling. Acids act on red lead. Nitric acid and glacial acetic acid first dissolve out the monoxide, leaving the dark puce oxide; on further boiling, this gradually dissolves and colourless solutions of the nitrate or acetate are formed. Hydrochloric acid when heated with red lead decomposes it with the evolution of chlorine and the formation of the chloride, which settles as the solution cools in the form of transparent needles, a very characteristic reaction of lead. Sulphuric acid boiled with red lead forms the sulphate, with the evolution of oxygen.

Red lead is a combination of the two oxides of lead, the monoxide, PbO , and the puce or dioxide, PbO_2 ; it is generally considered that they are present in the proportion of two equivalents of the first to one of the second, red lead, therefore, having the formula Pb_3O_4 , the percentage composition being—

Lead monoxide, PbO ,	. . .	64.5
Lead dioxide, PbO_2	. . .	35.5
		100.0

There is reason for believing that Pb_3O_4 does not accurately represent the true composition of red lead; for, although the proportions of the two oxides is about that given in the above analysis, it is probable that the whole of the monoxide present is not combined with the dioxide as red lead, but that some of it is in the free condition; this free oxide is not distinguishable from the combined oxides by treatment with acids, but, by treating with a 10 to 12 per cent. solution of lead nitrate, it is quite possible to extract 16 to 31 per cent. of free oxide, while the purified red lead thus obtained contains 25.4 to 25.7 per cent. of dioxide.*

* Lowe, *Dingl. Polytech. Journ.*, vol. 271, pp. 472-477.

The formula of red lead would then be Pb_4O_5 , which is that assigned to it by Phillips and other authorities. Percy* gives the following analysis of red lead:—

Lead monoxide, PbO ,	80·54 per cent.
Lead dioxide, PbO_2 ,	18·89 „
Ferric oxide, Fe_2O_3 ,	·19 „
Copper and silver,	trace
	<hr/>
	99·62

which corresponds to the formula $4 PbO, PbO$, or Pb_5O_6 .

Both Pb_3O_4 and Pb_4O_5 are known; the former is much easier to prepare than the latter, and the latter can only be made by repeated oxidation of the monoxide. A little free monoxide is desirable in red lead, as then the colour is not so readily liable to spoil by over-oxidation.

As a pigment red lead is very useful, it mixes very well with linseed oil, and takes from 8 to 9 per cent. of it to grind into a stiff paste. It exerts a powerful drying action on the oil; hence, paint containing red lead dries very quickly; on this account, also, red lead mixed with linseed oil is largely used as a lute and packing for steam pipes and joints of all kinds. It possesses good covering and colouring power, and is capable of resisting all ordinary atmospheric influences, although it is liable to be discoloured by sulphuretted hydrogen as is the case with all lead pigments. It may be mixed with nearly all pigments, the only exceptions being those containing sulphur, such as ultramarine, cadmium yellow, &c.

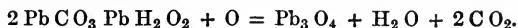
ASSAY AND ANALYSIS OF RED LEAD.—Red lead should be assayed for colour, fineness, and body in the usual way. It is rarely adulterated; but if so, it is usually by the oxide of iron reds. The quantity of red lead in such an adulterated sample can be ascertained by taking 2 grammes and boiling with nitric acid until it is thoroughly decomposed; the insoluble matter can be filtered off and its amount ascertained by weighing it; to the solution, which is colourless if the red lead be pure, but yellow if there is any iron present, a little dilute sulphuric acid is added, and a precipitate of sulphate of lead obtained; this is filtered off, washed, dried, and weighed in the usual manner. The weight multiplied by 0·955 gives the amount of red lead in the sample. The solution from the lead sulphate can be tested for iron, &c., by the usual tests.

* Percy, *Metallurgy of Lead*.

ORANGE LEAD.

This pigment is identical in composition with red lead, but is rather paler in colour and lighter in weight. To make it, white lead is placed in a furnace similar to a red lead furnace, and heated to a low red heat for from 24 to 48 hours, or until the mass has acquired the desired red tint. During this operation the white lead loses its carbonic acid and water, while it takes up oxygen from the air which passes through the furnace.

The change is shown in the following equation :—



In washing white lead a scum collects on the top of the washing waters; this is collected and made into orange lead, and gives a brighter and more bulky product than dry white lead. Orange lead has a slightly paler colour than red lead, is more voluminous and of lower specific gravity, which is about 6.95. In its composition and properties it is identical with red lead, and it is used for very similar purposes.

RED OXIDE, INDIAN RED, AND IRON REDS.

Ferric oxide, $\text{Fe}_2 \text{O}_3$, the red oxide of iron, is the basis of a very large number of red pigments which are sold under the names of rouge, light red, Indian red, red oxide, Venetian red, purple oxide, scarlet red, &c., which are all red pigments of varying shades of colour. In the hydrated form, ferric oxide also forms the colouring principle of the ochres, siennas, and umbers. The red oxides are valued very highly as pigments, on account of their generally fine colour and their permanence.

Ferric oxide occurs naturally in a variety of forms in the minerals hæmatite, specular iron ore, limonite, &c., in which it is nearly chemically pure. As a rule, they are too dark in colour, and too hard to be used as pigments; but, occasionally, deposits of oxide of iron are found of sufficient brilliance to be used as a pigment—*e.g.*, the Warton oxide named below. Indian red was originally found native, but is now mostly of artificial manufacture. Such substances as red ochre, yellow ochre, red raddle, umber, &c., owe their colour to oxide of iron, but they contain many other bodies.

These pigments are prepared both from natural and artificial sources. Before entering into the details of their preparation a

few words about the oxides of iron and their properties will be of use in understanding the subject.

There are three principal oxides of iron, viz. :—

Ferrous oxide, the green or protoxide, Fe O .

Ferric oxide, the red or peroxide of iron, $\text{Fe}_2 \text{O}_3$.

Triferric tetroxide, the black or magnetic oxide, $\text{Fe}_3 \text{O}_4$.

Ferrous oxide (iron monoxide, protoxide of iron, as also, from its colour and the colour of its salts, the green oxide), Fe O , is not known in the free condition. When a solution of caustic soda or of caustic potash is added to a solution of a ferrous salt a green precipitate of the ferrous hydroxide, $\text{Fe H}_2 \text{O}_2$, is obtained; this, when exposed to the air, rapidly oxidises and passes into the ferric compound, the change being accompanied by a change of colour from green to red; even when kept under water this change goes on, although slowly; on heating it changes to the ferric oxide. Except in a few rare minerals ferrous oxide is not known to exist naturally. Ferrous hydroxide is soluble in all acids, with the formation of the corresponding ferrous salt; these salts are only stable when in the dry condition, when dissolved in water they gradually change into the ferric salts, and usually a small quantity of ferric oxide is formed at the same time.

Ferric oxide (iron trioxide, sesquioxide of iron, peroxide of iron), $\text{Fe}_2 \text{O}_3$, is the most important of the three oxides of iron. It is found in great abundance in nature in a great variety of forms, some of which have been noticed above. It generally occurs in a nearly pure state, and is then used as an ore of iron; at other times it is found mixed with earthy and other substances in variable quantities, such bodies are used for several purposes; some of them, which have been named above, as pigments. It is usually of a dark red colour, although some forms are nearly black. When it occurs in a hydrated condition, as in limonite, or as it is in yellow ochre, it has a brownish-yellow or brown colour. Ferric oxide is soluble in acids, easily in strong hydrochloric acid, or a mixture of nitric and hydrochloric acids; it is not so readily soluble in sulphuric or nitric acids; with these acids it forms the ferric salts; but the degree of solubility is very variable, some forms being almost insoluble, while others are freely soluble. It is perfectly stable, and can be exposed to the air for any length of time without change. When a solution of caustic potash or soda or ammonia is added to a solution of a ferric salt a brownish-red, flocculent precipitate of the ferric hydroxide, $\text{Fe}_2 \text{H}_6 \text{O}_6$, is obtained; on being heated to a low red heat this loses its water and passes into the oxide, $\text{Fe}_2 \text{O}_3$.

Triferric tetroxide (magnetic oxide of iron), Fe_3O_4 , is found naturally in large quantities as the mineral magnetite, the natural loadstone; this is used as an ore of iron; it is not readily soluble in acids, and its solution contains both ferrous and ferric salts.

A fourth oxide, **ferric anhydride**, Fe_2O_3 , is known in the form of a compound salt of potassium, corresponding to the chromate of potassium; it is not, at present, of practical importance.

MANUFACTURE OF OXIDE REDS.—These are obtained, as stated above, from (a) natural and (b) artificial sources.

(a) *Preparation from Natural Oxide of Iron.*—The preparation of oxide reds from the iron minerals is comparatively simple. The mineral is first ground in an edge-runner grinding mill so as to reduce the large masses to small pieces; then these are sent several times through a roller mill, until they are fine enough, or they may be put through a horizontal stone mill fitted with a hopper for levigating and the ground pigment levigated to free it as much as possible from grit; after this, the levigated material requires to be dried before it can be sent out. Descriptions of grinding mills, levigating and drying processes will be found in subsequent chapters.

As a rule, the natural oxide reds are fairly pure products; some analyses will be found on p. 109. They are generally dark, and are mostly sold as Indian red and red oxide. They are excellent and very permanent pigments.

(b) *Preparation from Artificial Sources.*—Oxide of iron reds are prepared from a variety of materials, some of which are obtained as waste products in other branches of manufacture, while others are used directly for making them. The manufacturer is able, within certain limits, to prepare any shade of red which is desired; the darker shades are much more easily prepared than the paler shades; the former may be almost chemically pure, but the paler shades can only be made from such bodies as the ochres, which only contain a comparatively small quantity of iron.

The artificial oxide reds are sold under a great variety of names. In some cases these originally showed the origin of the pigment when it was first introduced, e.g., Indian red and Venetian red; while others, such as purple oxide, light red, and scarlet red are indicative of the shade of colour. The names, as now used, are usually indicative of the shade of the red, thus rouge, colcothar, scarlet red, and Turkey red are bright reds; Venetian red is a pale red; light red is rather darker, but is usually paler

than those above enumerated ; Indian red and red oxide are dark reds ; while light and dark purple oxides are of a dull violet hue.

The processes which are used in the preparation of oxide reds may be grouped under two heads :—

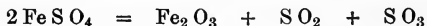
1st. Dry Processes.

2nd. Wet Processes.

In the first group the reds are made by heating an iron compound.

In the second, a precipitate of iron is thrown down from solution, and is then usually heated to convert it into the red.

1st. **DRY PROCESSES.**—(a) **From Copperas.**—The principal material used in the preparation of these reds by the dry processes is copperas, ferrous sulphate. This iron salt is made in very large quantities by exposing iron pyrites to the oxidising action of the air, neutralising the acid solution of sulphate thus obtained by means of scrap iron and then crystallising out the ferrous sulphate so formed. Copperas, ferrous sulphate, forms large, pale green crystals, which have the formula $\text{FeSO}_4, 7\text{H}_2\text{O}$. On exposure to the air they are liable to oxidise and to form a brown crust of the ferric oxide. Heated at about 120°C . they lose 6 of the 7 molecules of water of crystallisation they contain, falling to a white powder in so doing ; at a higher temperature they lose the seventh molecule of water. Copperas dried by heat is much used as a drier in varnish making. Partially-dried copperas, when heated to a white heat, or even to a lower temperature, is decomposed ; it loses its sulphur trioxide, while a residue of ferric oxide remains ; some of the sulphur trioxide is, however, decomposed into sulphur dioxide, the oxygen it loses going to the iron. The change is expressed in the equation—



When carried out on a large scale, the copperas is rarely thoroughly dried, so that the water it contains passes off with the sulphur oxides, and forms with them a brownish fuming liquid known as Nordhausen or fuming sulphuric acid ; in fact, this was the first process by which sulphuric acid was made, but it is now displaced by the English method ; the iron oxide which is left behind is sold for various purposes under the name of rouge or colcothar.

The process may be carried on with a view of obtaining the acid as the principal product and the oxide as a bye-product, or

the oxide may be the principal product and the acid the by-product, as is the case when copperas is calcined.

When the process is carried on with a view to obtain the acid which is evolved, the operation is generally done in cast-iron stills which are fitted with suitable condensing arrangements. The stills are heated to a red heat; after the evolution of the acid vapours has ceased, the still is allowed to cool, and the residual oxide ground with water to wash it and grind it as fine as possible; then it is dried and sent out as rouge or colcothar or scarlet oxide, &c. The oxide must be washed to free it from all traces of the acid, which would reduce its value as a pigment if left in.

The usual plan is to calcine the dried copperas, either with or without previous drying, in a form of muffle furnace, such as is shown in Fig. 16, which may be arranged with a view to collecting the acid gases evolved or to allow them to pass away without being collected, as is perhaps the most common plan; but in view of the value of sulphuric acid, it is worth while to collect and manufacture the acid gases into the acid, especially if the oxide manufacture be carried on so far from an acid works that the cost of the sulphuric acid required for other operations in the colour works becomes an important item.

By regulating the temperature at which the calcination is carried on, and also its duration, the shade of the resulting oxide may be modified to suit the requirements of the colour maker; thus if carried on at a dull red heat a bright shade of red is obtained; if at a red heat, a darker red; while at a white heat, the oxide will take a dark violet shade. The same effects may be produced by prolonging the calcination at a lower temperature, but the results are usually not so good. During the calcination it is necessary to take out samples from time to time to see how the operation is proceeding. When the mass has acquired the right shade the operation is stopped by drawing the furnace fire, and the furnace and its contents are allowed to cool down; or the oxide may be withdrawn while still hot, leaving the furnace in a condition to take another charge without loss of time and with some saving of fuel.

Although it is not necessary to add anything to the copperas in order to produce the oxide, some makers add a small quantity of salt, about 2 to 3 lbs. per cwt. of copperas; other makers add sulphur; but there cannot be much advantage in adding these bodies, especially the latter. The salt may act by increasing the bulk of the resulting oxide and thus tending to brighten the shade somewhat. When these bodies are added it is necessary

that the oxide be very carefully washed before it is sent out, as if any salt, &c., be left in it will interfere very materially with the use of the oxide as a pigment.

Messrs. Leech & Neal have patented the use of a kiln constructed very similar to a brick kiln, the gases evolved from which are passed into a lead chamber, where the sulphuric acid they contain is condensed, while the sulphurous acid passes into a column with water and scrap iron, dissolving the latter and forming ferrous sulphate, which is used for another batch of oxide.

Lavender describes in a patent a method of preparing oxide from the waste liquors of iron galvanisers which, if they have used sulphuric acid for pickling the iron, contain sulphate of that metal, by passing superheated steam through them, thus driving off the water and excess of acid and drying the sulphate, which

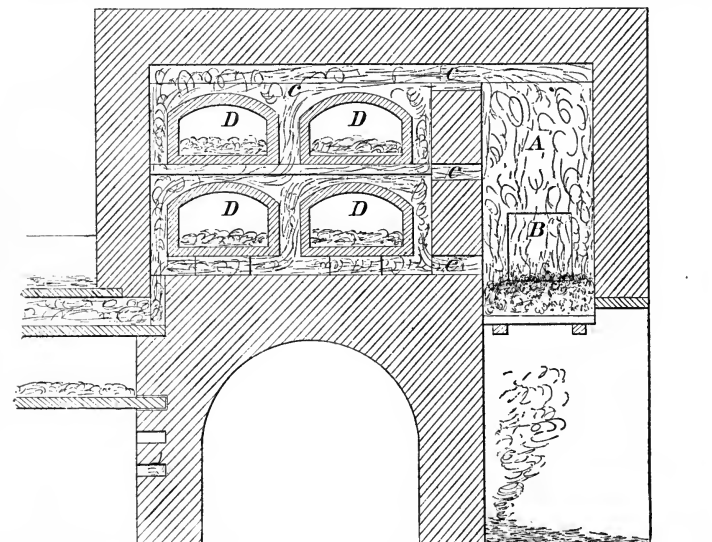


Fig. 16.

is then calcined in kilns so built that the gases evolved can be condensed in lead chambers.

In another patent *Madge* has described a furnace and process for preparing oxide from copperas. The furnace is shown in Fig. 16, and is of the muffle form, with arrangements for collect-

ing and condensing the sulphur gases evolved. The copperas is first dried on iron plates heated by the waste heat from the muffles; then, after drying, it is transferred to the muffles and further calcined to oxide, which is then finished as usual.

The oxide yielded by the above processes is fairly pure and mostly of a dark red shade, which, as has been mentioned above, may be varied at will to some extent, but the pale shades cannot be obtained in this way.

(b) **From Ochres.**—By calcining ochres, an operation which is carried on on a large scale, reds are obtained which vary in tone very much and to a greater extent than is possible in the case of the oxides prepared as above described from copperas. The process was patented as early as 1794 by *Atkinson*. The furnace for calcining ochres varies in form at different works; in some places it is simply a stone slab or iron plate placed over a fire; in others some form of muffle furnace is used; indeed, almost any form of furnace may be used.

The ochres should be ground and levigated before they are calcined, as the red obtained from ground ochres is better than that obtained from unground ochres. For Venetian reds about 8 hours at a low red heat is required; light reds require about 10 hours; Indian reds about 12 hours; while purple reds require 16 hours. With higher temperatures less time is required. During the progress of the calcining test-samples should be taken out from time to time to see how it is proceeding, and when the red has assumed the required shade it must be withdrawn from the furnace. As soon as it is cold it is ready for the market, provided it has been ground and levigated before heating, otherwise it must be ground and levigated before it is fit to use as a pigment.

The oxide of iron exists in the ochre in a hydrated condition (see *Ochres*, p. 133), and this has a brownish tone. On calcining, this water of hydration is driven off, and the oxide, becoming converted to the anhydrous condition, turns red.

The iron reds made from ochres are necessarily impure, as the oxide of iron is associated with silica, alumina, lime, &c., their composition varying with that of the ochres from which they are made. Some analyses of these reds will be found on p. 109.

2nd. **WET PROCESSES.**—A very large proportion of the oxide reds now sold are prepared by a combined precipitation and calcining process which can be grouped briefly as “wet processes.”

In a large number of metallurgical operations liquors containing iron are produced in large quantities; formerly these

were thrown away as useless, but now the iron they contain is recovered in the form of red oxide, which is used as a pigment. Processes for extracting the iron from these liquors have been the subject of numerous patents, some of which have been worked on the large scale, while others have not gone beyond the experimental scale; some are for the actual process, while others are for the plant which is required for the purpose, and some are for both process and plant. It is not necessary to describe these in detail, but an outline of the principal processes will be given.

In galvanising or tinning iron goods to preserve them from the rusting action of the atmosphere the iron goods are first dipped into dilute sulphuric or hydrochloric acid to clean them free from any oxide before placing them in the zinc or tin bath; necessarily the acid liquor will become charged with iron to a greater or less extent; formerly this acid liquor was thrown away, but galvanisers have been compelled to adopt some plan of treating it as the various local authorities interested objected to its discharge into drains and watercourses. The iron is recovered by precipitating it in the form of oxide by the addition of an alkaline solution. For this purpose soda crystals, caustic soda, ammonia, ammonia carbonate, or lime may be used; the latter is the cheapest, but its use requires some care, as, if used in excess (which may easily happen), the excess will find its way into the drains or watercourses, where its presence is rather objectionable. By any of these bodies the iron is practically precipitated in the form of oxide; as a bye-product there will be obtained some alkaline compound, the nature of which will depend upon the nature of the alkali used and of the acid employed in the galvanising operation. If soda is used, either chloride or sulphate of soda will be formed in the liquors; these may be thrown away, as the quantity obtainable is not worth recovering; if ammonia is used (and for this purpose the crude ammonia liquor of gas works may be used), either ammonia chloride or sulphate will be formed, from which ammonia may be recovered. When lime is used, either chloride or sulphate is obtained; in the former case it will pass away in solution, while in the latter it will pass into the precipitate and will modify the shade of the resulting pigment.

The general method of procedure is as follows:—The liquors are run into tanks and the acidity of them is destroyed by adding scrap iron; then the alkaline liquor is added in sufficient quantity to precipitate the whole of the iron; the precipitate is collected on filters, dried by any convenient means, and then calcined in a furnace. If a Venetian red is wanted, after pre-

cipitating, a quantity of sulphate of lime is added, so that there shall be about three or four parts of sulphate to one of oxide; this addition is generally only necessary when the iron liquors contain hydrochloric acid and not sulphuric acid.

The use, during recent years, of large quantities of Spanish cupreous pyrites in the manufacture of sulphuric acid, and the extended use of wet processes for the extraction of the copper from the residual oxide left behind after the sulphur has been burnt off, has placed at the disposal of the colour maker new and cheap sources of waste iron liquors. In the manufacture of sulphuric acid the pyrites is burnt in kilns, the sulphurous acid gas evolved is sent into lead chambers to be converted into sulphuric acid, while the burnt ore is heated in a suitable furnace with salt, which converts all the copper and some of the iron into chlorides. The furnaced mass is now dissolved in water, scrap iron is thrown into the liquors thus obtained to precipitate the copper, while the iron passes into solution; the iron liquors thus obtained are a waste product so far as the copper extractor is concerned, but the colour maker can use them for making red oxide.

The iron in these liquors generally exists in the form of chloride and sulphate; from them the oxide is precipitated by adding lime, after which the precipitate is collected, dried, and calcined in the usual way. The oxides so obtained nearly always contain sulphate of lime, which is precipitated along with the iron on adding the lime to the iron liquors; this sulphate of lime tends to make the oxide of a lighter shade than it would otherwise be. During the last few years many patents have been taken out for treating these waste iron liquors for oxide making, in the specifications of which full details will be found of the processes adopted.

PROPERTIES OF RED OXIDES.—Red oxide pigments form red powders of various shades, from a pale red to a dark violet, the specific gravity of which varies from 2·6 to 3·1; they are quite insoluble in water, and more or less insoluble in acids. If the oxide has been made at a low temperature, as for instance rouge, it will dissolve in strong hydrochloric acid; if it has been made at a higher temperature, Indian red for example, it is not readily soluble in hydrochloric acid, and requires a mixture of that acid and nitric acid to effect its solution; while the purple oxides which have been prepared by calcining at a very high temperature are very insoluble bodies, and require to be treated with a mixture of sulphuric, hydrochloric, and nitric acids before they will dissolve. This point regarding the

solubility of oxide reds should be borne in mind when making an analysis of these bodies. Of course it is only the pure oxides which are soluble, those made from ochres always yield an insoluble residue of some kind.

As a pigment, red oxides are perfectly permanent under all conditions, and are among the most permanent pigments a painter can use. They mix perfectly with all pigments without either affecting them in any way or being affected by them. They do not mix as well with oil as red lead, take about 10 per cent. of oil to grind into the usual stiff paste, and do not act as driers.

ANALYSIS AND ASSAY OF RED OXIDES.—From what has been said above as to the methods of preparation of red oxides it will have been gathered that these bodies are of very variable composition; some are nearly pure oxide, others contain calcium sulphate, while others are much more complex, containing silica, alumina, calcium, &c. In technical work it is rare that the absolute purity of a body is an essential feature, and this applies, as a rule, to pigments particularly; with them purity is not essential, provided the impurity is of such a character as will not affect the use of the pigment as a pigment; for example, sulphate of lime may be present, but not caustic lime, as the former will not, beyond making the shade lighter, affect the pigment injuriously, while the latter will. It is rarely, therefore, that an analysis of a pigment is required, and this is particularly the case with red oxides.

When an analysis is required of an oxide red the following scheme may be adopted:—

Water.—Weigh 2 grammes into a watch-glass, and heat in a hot oven to a temperature of about 120° C. until there is no further loss of weight. This gives the hygroscopic water. For the combined water weigh 2 grammes into a crucible, and heat to a red heat over the Bunsen burner for about one hour, then, after allowing to cool, weigh; the loss of weight is the hygroscopic *plus* the combined water.

Next weigh into a beaker 5 grammes, and heat with a mixture of hydrochloric and nitric acids until the red is completely decomposed; then evaporate the solution to dryness, treat the dry mass with a little dilute hydrochloric acid, filter off into a 500 cc. flask, wash well with water, and fill the flask up to the mark. This solution is used for the various tests given below. The residue on the filter is the silica, barytes, &c., which can be dried and weighed.

For the *iron, alumina, &c.*, take 200 cc. of the above solution,

ANALYSES OF RED OXIDE OF IRON PIGMENTS.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.
Ferric oxide, Fe ₂ O ₃ , . . .	96·00	43·59	94·71	30·59	98·5	82·25	9·60	43·82	63·91	9·64	92·72	5·17
Alumina, Al ₂ O ₃ , . . .	1·24	...	1·6	1·42	28·30	·60	5·05
Silica, SiO ₂ , . . .	1·49	...	2·8	...	1·2	...	9·28	23·16	...	22·01	1·36	4·46
Calcium carbonate, CaCO ₃ ,	·39	80·04	3·15	3·31	63·86	...	62·55
Calcium sulphate, CaSO ₄ ,	53·94	...	53·60	·10	5·52	1·00
Barytes, BaSO ₄ ,	21·11
Water, combined, . . .	1·35	1·3	·69	1·70	·3	10·40	...	1·07	10·65	4·15	·39	20·14
Water, hygroscopic,	1·05	·14	14·05	...	7·35	...	·38	·50
Organic matter, . . .	trace
Magnesia, MgO,	trace	...	trace	trace	·33	...	1·00
	100·08	99·88	100·33	99·94	100·00	100·00	100·44	99·88	99·58	99·99	99·99	99·87

I. Natural hematite from near Ulverston.

II. Manufactured Indian red.

III. Natural Indian red from India.

IV. Scarlet red.

V. Purple oxide.

VI. Rouge.

VII. Red chalk from Speeton, Yorkshire.

(Clapham, *Chem. News*, 1862; p. 313).

VIII. Indian red.

IX. Indian red made from Derbyshire ochre.

X. Spanish brown.

XI. Indian red.

XII. Venetian red.

add carbonate of soda until the solution is neutral, then ammonium acetate; boil, filter, wash and dry, and weigh the precipitate; this consists of oxide of iron, alumina, and, in some rare cases, phosphoric acid, but this may be neglected, as a rule, in iron reds. The iron may be estimated in another portion of the original solution by a volumetric test and the amount of alumina calculated from the two results. The filtrate from the precipitate is mixed with a small quantity of ammonium sulphide to precipitate any manganese, this precipitate being collected, dried, and weighed. To the filtrate is added ammonium oxalate to precipitate the calcium, which is filtered off, dried, and weighed. To the filtrate from this, sodium phosphate is added to precipitate the magnesium, if present.

For the sulphate which is present 100 cc. of the original solution are taken and some barium chloride is added; the precipitate of barium sulphate is filtered off, dried, and weighed.

For fuller details as to the method of carrying out this scheme, works on quantitative analysis, such as that of Professor Sexton, published by Griffin & Co., should be consulted.

The analyses on p. 109, which, with the exception of Nos. 3 and 7, have been made by the author, will show the composition of the iron reds in common use as pigments.

A pigment must possess two properties, good colouring power and body. As the iron reds are so variable in their composition it follows that in these two particulars they will vary also; for these two properties they should be assayed, the methods of doing which will be found detailed in the chapter on assaying pigments.

ANTIMONY VERMILION.

This pigment, also known as antimony orange, is very largely used for colouring india-rubber; for other purposes it is not used as extensively as it might be.

It is the sulphide of the metal antimony and has the formula Sb_2S_3 . This body occurs naturally as the mineral stibnite or antimony glance of a lustrous black colour; when ground up it is known as black antimony, and is used for various purposes in the arts, one being as a source for the manufacture of antimony vermilion.

PREPARATION OF ANTIMONY VERMILION.—*Murdoch*, in 1847, patented a process for the preparation of antimony vermilion and a similar process was the subject of a subsequent patent taken out by *Clark*. The pigment can be made in

two modifications, orange and red; the former by precipitation with sulphuretted hydrogen, the latter by other agents.

(a) **Orange Antimony.**—Murdoch dissolves the black antimony in hydrochloric acid; during the operation some sulphuretted hydrogen is evolved and may be used for precipitating another solution previously made; so as to form a solution of antimony chloride, which is concentrated till it has a strength of 19° Tw.; through it is then passed a current of sulphuretted hydrogen gas which precipitates the sulphide of antimony as an orange powder, which, after being well washed and dried, is ready for use.

Fig. 17 shows a convenient form of apparatus for precipitating antimony vermilion. A is a vessel made of wood, lined with lead, and fitted with a lid which, while being removable to admit of the sulphide of iron used for the preparation of the gas, can

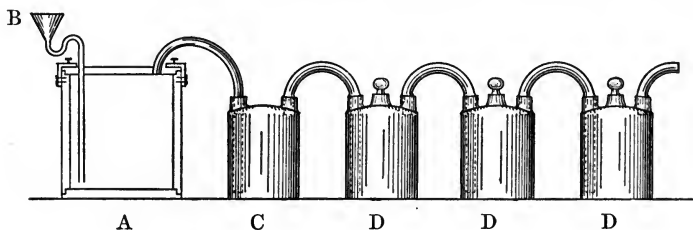


Fig. 17.—Apparatus for making antimony vermilion.

yet, by means of india-rubber joints, be made gastight; B is a funnel for the admission of acid; C is a two-necked bottle filled with water to wash the gas as it comes over; D, D, D, are three-necked bottles (whose construction is shown in the drawing), containing the solution of antimony through which the gas is passed. The most convenient method of preparing the gas is by the action of dilute sulphuric acid on sulphide of iron.

By varying the strength of the antimony solution the shade of the resulting pigment can be varied to some extent; thus, a solution of 19° Tw. gives an orange-red; one of 40° Tw., a reddish-orange; while one of 52° Tw. gives an orange colour. When strong solutions are used the precipitate is, however, liable to contain free sulphur, which is sometimes objectionable as it may cause decolourisation of the pigment.

(b) **Scarlet Antimony.**—1. *Mathieu Plessy Process.*—This consists in precipitating a solution of chloride of antimony with a solution of sodium thiosulphate (hyposulphite of soda) under

certain conditions. A solution of chloride of antimony of 40° Tw. is prepared. The ordinary commercial chloride is a liquid of about 1.26 (52° Tw.) specific gravity; if this is diluted with water in the proportion of 5 vols. of the chloride to 2 vols. of water, a solution of about 40° Tw. will be obtained. A solution of sodium thiosulphate of 40° Tw. is also prepared; this will take about 14½ ozs. weight of the salt to 25 ozs. measure of water.

7½ gallons of the thiosulphate solution are taken, and into them are poured 3 gallons of the antimony solution; a black precipitate forms at first, but this disappears rapidly. The liquid mixture is now gently heated; when the temperature reaches about 78° to 90° F. a yellow precipitate begins to form; as the temperature increases the colour changes, passing through various shades of orange till at about 130° to 140° F. it acquires a scarlet-red colour; the operation is now stopped and the mass allowed to cool down; when cold, the clear supernatant liquor is poured off, water containing a trace of hydrochloric acid is poured on to the precipitate, which is stirred up; after which the mass is allowed to stand to settle, the top liquor poured off, and the colour washed with water two or three times; it is now dried at a low temperature (about 140° F.), and when dry is ready for use.

During the process of precipitation a very considerable evolution of sulphur dioxide gas takes place; therefore, the operation should be carried on in a place and under conditions where the gas cannot cause inconvenience.

2. *Wagner's Process*.—4 lbs. of tartar emetic and 3 lbs. of tartaric acid are dissolved in 18 lbs. of water, and the solution heated to 140° F., a solution of sodium thiosulphate of 40° Tw. added thereto, and the mixture heated to 180° F. The red is gradually precipitated, and when fully formed is washed with water and dried.

In drying antimony vermilion it is important that the temperature be kept low, and not be allowed to rise above 160° F.

The colour of the scarlet antimony powder is rather dull, but it becomes bright when mixed with oil or water.

PROPERTIES OF ANTIMONY VERMILION.—Antimony orange is a light, bulky, orange-coloured powder, while antimony vermilion is a scarlet powder rather heavier than the orange variety. Both pigments have practically the same properties; they are not attacked by dilute acids, but strong nitric acid gradually decomposes them, with the formation of white antimonious oxide and sulphuric acid. Strong hydrochloric acid has little action in the cold, but when boiling

gradually dissolves them with the formation of chloride of antimony and evolution of sulphuretted hydrogen. Caustic soda and potash when boiled dissolves the colour, which is re-precipitated as an orange precipitate on the addition of an acid; ammonia has little action; lime has a similar action to soda.

Both the orange and red forms are rather dull in the pulverulent state, but when mixed with oil or water they become bright; being opaque they have a good body or covering power, and mix well with oil, but cannot be used with alkaline vehicles, like lime or silicate of soda, which have a decolourising action. They are unalterable by air or light, or by deleterious atmospheric agents.

They can be mixed with all those pigments which are unaffected by sulphur.

COMPOSITION OF ANTIMONY VERMILION.—

Pure sulphide of antimony, Sb_2S_3 , has the following percentage composition:—

Antimony,	71.42
Sulphur,	28.28
		100.00

The antimony pigments are liable to contain free sulphur, especially those which are made with sulphuretted hydrogen. The following is an analysis of an orange antimony:—

Moisture,	2.200	per cent.
Sulphur,	40.557	„
Antimony,	56.990	„
		99.747	

from which it will be seen that the sulphur is greatly in excess of that required by theory, so that some of it must be in the free condition.

The red antimony vermilion approach more closely to the theoretical composition, as will be evident from the following analyses:—

	a.	b.
Water, 1.1	4.227
Sulphur, 26.7	27.103
Antimony, 72.2	68.670
	100.0	100.000

the latter analysis by the author is of an English made sample, the other analyses are taken from a foreign work on pigment-making.

The presence of free sulphur in these pigments is likely to be a cause of want of permanence when used as a pigment.

ANALYSIS AND ASSAY.—For practical purposes it is not necessary to make a complete analysis of antimony vermilions. They are liable to adulteration by red lead, oxide of iron, or chrome orange. Red lead would be shown by the colour darkening when treated with hydrochloric acid, and, after solution, by crystals of chloride of lead separating out on cooling, and the application of the usual tests for lead. Oxide of iron can be distinguished by the solution in hydrochloric acid having a yellow colour and giving the characteristic tests for iron; chrome orange can be detected by the colour of the acid solution being green and giving the tests for lead and chromium.

Antimony vermilions should be assayed for colour, both in the form of powder and when mixed with oil, and for covering power by the usual methods.

BRILLIANT SCARLET is the name given to the iodide of mercury, $Hg I_2$, prepared by carefully precipitating a solution of mercuric chloride with a solution of potassium iodide; it has a brilliant scarlet colour, but is very fugitive. It is rarely used as a pigment.

DERBY RED is the basic chromate of lead; its preparation and properties will be found on p. 116, *et seq.*

The **CHROMATE OF MERCURY** has been used as a red pigment and is prepared by precipitating a solution of mercuric chloride with potassium chromate; its cost and want of permanence has caused it to become obsolete as a pigment.

The **CHROMATE OF SILVER** has been proposed as a pigment; it has a dark red colour and is prepared by precipitating a solution of silver nitrate with a solution of potassium chromate. It is costly and fugitive.

The **CHROMATE OF COPPER**, a dark red coloured body prepared by precipitating solutions of copper with potassium chromate, has also been suggested, and probably used on a small scale, as a pigment; but it is fugitive, and, therefore, cannot be recommended for this purpose.

MAGNESIA PINK, prepared by calcining a mixture of magnesia and cobalt nitrate, has been little used; it has but a pale colour and little body, although probably permanent.

CHAPTER IV.

YELLOW AND ORANGE PIGMENTS.

THERE is a fairly large list of yellow and orange pigments derived from the vegetable, animal, and mineral kingdoms, the most important being the chromes and ochres; the others are only used in small quantities.

THE CHROMES.

The chromes, as they are generally called, are a very important group of pigments varying in colour from a pale yellow through deep yellow, orange to bright red, and sold under a variety of names—primrose-chrome, lemon-chrome, chrome-yellow, orange-chrome, scarlet-chrome, chrome-red, Derby-red, American-vermilion, &c. The base of all these chrome pigments is the chromate of lead, Pb Cr O_4 , and its basic derivative Pb O, Pb Cr O_4 .

Chromate of lead is capable of existing in the form of acid, normal and basic modifications; to the colour maker, only the last two are of any interest.

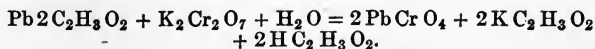
The normal chromate of lead is a deep-yellow coloured body having the composition

Lead,	63.99 per cent.
Chromium,	16.23 "
Oxygen,	19.78 "
		<hr/>
		100.00

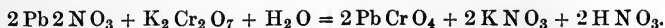
or

Lead oxide, Pb O ,	68.93 per cent.
Chromium oxide, Cr O_2 ,	31.07 "
		<hr/>
		100.00

It is obtained as a bright yellow precipitate by adding a solution of bichromate of potash to one of acetate of lead; the reaction is shown in the following equation:—



Nitrate of lead may be used instead of the acetate, when the reaction becomes



From the above equations the equivalent quantities of the two compounds can be calculated, and are as follows:—650 parts of lead acetate or 662 parts of lead nitrate are equal to 295 parts of potassium bichromate, or 100 parts of lead nitrate require 44·5 parts of potassium bichromate, while 100 parts of lead acetate require 38·9 parts of potassium bichromate to precipitate them.

Lead chromate is insoluble in acetic acid and water, but soluble in moderately concentrated nitric or hydrochloric acids. When treated with a large excess of caustic potash or soda it dissolves, but when heated with a small quantity of the alkalis it is converted into the basic chromate, Pb_2CrO_5 . Heated alone it first turns reddish-brown, and, finally, becomes greenish-grey with evolution of oxygen, while a mixture of the oxides of lead and chromium are left behind.

It has a specific gravity of 5·653.

The formation of the basic chromate from the normal chromate is shown in the equation



It is a scarlet-red powder of somewhat crystalline structure, with a specific gravity of 6·266; by friction it loses its crystalline form and changes colour, becoming orange; in other properties it resembles the normal chromate. It has the following composition:—

Lead,	75·75	per cent.
Chromium,	9·61	„
Oxygen,	14·64	„
		<hr/>	
		100·00	

or

Lead oxide, PbO ,	81·61	per cent.
Chromium trioxide, CrO_3 ,	18·39	„
		<hr/>	
		100·00	

Both the normal and basic chromates when boiled with strong sulphuric acid are decomposed, lead sulphate and chromium sulphate being formed and oxygen evolved. Strong hydrochloric

acid on boiling dissolves them, forming a green solution of lead and chromium chlorides, from which, on cooling, the lead chloride separates out, and the chlorine is evolved. When boiled with solutions of the alkaline carbonates, the chromates are decomposed, white carbonate of lead being formed and a solution of the alkaline chromate obtained. When boiled with solutions of caustic soda or potash the lead chromates dissolve; on adding acetic acid to this solution a yellow precipitate of the normal chromate is obtained.

MANUFACTURE OF LEAD CHROMES.—In commerce the pigments having chromate of lead as the base are met with in a very great variety of shades from a very pale primrose-yellow to a deep red; as a rule, the deep shades are almost chemically pure, but the pale shades are obtained by mixing the pure chromate with the requisite quantity of a white base, such as sulphate of lead, barytes, gypsum, &c.; what are called "pure chromes" in the trade contain sulphate of lead, while the common chromes contain this body with barytes or some other white base in addition.

The preparation of these pigments may be grouped under three heads:—

- 1st. Preparation of chrome-yellows.
- 2nd. Preparation of chrome-oranges and scarlets.
- 3rd. Preparation of chrome-reds.

The same plant may be used in the preparation of all these chromes.

The best form is that shown in Fig. 18 which, in its simplest form, consists of three tubs made of hard wood; one of these, the largest, C, is placed on the floor, while the other two are placed above it on a small platform, P. In these two tubs (D D of the Fig.) are dissolved the salts used, the bichromate of potash and other precipitants in one, the lead salt in the other; care being taken always to use the same tub for the same material. These tubs may measure 3 ft. 6 in. by 2 ft. 6 in.; they will hold about 107 gallons each. The larger tub, C, may measure about 4 ft. in diameter by 3 ft. high, and will hold about 176 gallons. In this tub the colour is formed, and may, therefore, be called the precipitating or colour tub. The contents of D D may be heated by an arrangement of steam pipes, S S, and the colour tub should also be provided with a steam pipe, so that its contents can be heated up if required. At the bottom of D D are plugs, on opening which

the contents can be run into the colour tub, C. For the purpose of running off the liquor from the precipitated colour in C, the latter is provided with a number of holes, H, H, H, H, at various heights in its side fitted with plugs, any one of which may be drawn out to permit the water or liquor to run away.

In a plant of this kind about 2 cwt. of chrome may be made at one batch. It is advisable to provide several such sets of plant, which may be arranged as shown in the drawing, in which case one of the solution tubs, D, may be used along with two colour tubs, C C.

1st. **PREPARATION OF CHROME-YELLOWS.**—The number of recipes which are in use for preparing chrome-yellows

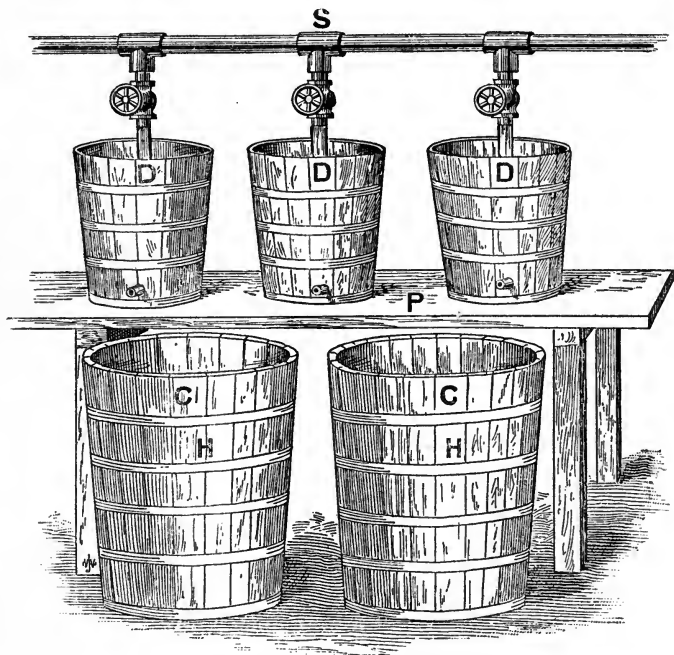


Fig. 18.—Plant for preparing chrome-yellow.

is legion. Most colour-makers will produce from 6 to 10 or 12 shades, and it is quite probable that the recipes in use in different works for producing what is nominally the same shade

differ very much. Under these circumstances it will be best to describe the production of a few of the more prominent shades, and point out how, by various modifications in the recipes, others can be obtained.

All the chrome-yellows are prepared by a comparatively simple and easily-conducted process of precipitation. These colours are admixtures of pure normal lead chromate, with either sulphate of lead (in which case the resulting colour is still called "pure") or with barytes, gypsum, or some other white base.

Sulphate of lead is produced along with the chromate by precipitation, using either sulphate of soda or sulphuric acid as the precipitant, while the barytes, &c., is added to the colour as it is being made.

The method of preparing the chromes is this:—The lead salt, either the acetate or nitrate, is dissolved in a tank, D, Fig. 18, with the necessary quantity of water; heat may be used to facilitate solution, if thought desirable, but the actual precipitation is done cold. In another tank, D, Fig. 18, is dissolved either bichromate of potash or bichromate of soda and sulphate of soda (Glauber's salt). As the commercial products are liable to be dirty, the solutions must be either filtered or allowed to settle in the tanks, and the clear supernatant liquor only used; when both solutions are ready they are run simultaneously into the precipitating tank C, Fig. 18, where the chrome-yellow is precipitated, and is allowed to settle to the bottom of the tank; the clear top liquor is run off by opening one of the plugs, H, fresh water run in, the whole stirred up and again allowed to settle, and the clear liquor run off. The washing is repeated, if thought necessary; for best qualities at least three washings should be given. After the washing the pulpy colour is thrown on to an ordinary felt filter, or put into the filter-press to extract as much water as possible, and then dried in a stove at as low a temperature as possible.

If barytes or gypsum be used to tone down the yellow to the required shade it is put into the precipitating tank C with a quantity of water, with which it is well mixed, so as to get a uniform milky mixture; then the two precipitating solutions, which have been prepared in the tanks D D, are run in, care being taken that the contents of tank C are thoroughly well agitated all the time; afterwards the colour may be finished as before. If the barytes, &c., is not properly mixed there is great liability for it to aggregate in lumps, and the proper shade is not obtained; besides the finished colour will be full of white masses.

“Pure” Lemon-yellow.

Lead acetate or nitrate,	100 lbs.
Bichromate of potash or soda,	25 „
Glauber’s salt (sodium sulphate),	35 „

“Pure” Chrome-yellow.

Lead acetate or nitrate,	100 lbs.
Bichromate of potash or soda,	30 „
Glauber’s salt (sodium sulphate),	21 „

“Pure” Deep Chrome-yellow.

Lead acetate or nitrate,	100 lbs.
Bichromate of potash or soda,	35 „

To obtain fine shades it is necessary to keep the lead in excess. Now, theory indicates that for 100 lbs. of lead salt 39 lbs. of potassium bichromate are required; in practice, however, it is found that if the full theoretical amount is used then the shade of the colour is affected, hence it is not advisable to use more than 35 lbs.; the above recipes have been based on this amount, so that in all, the lead is in excess. The weaker the solutions used for precipitating, the finer will the resulting pigment be.

The shade of the pigment obtained depends upon the proportion between the two precipitants, bichrome and Glauber’s salt; the more sulphate there is present the paler will be the shade of yellow obtained, a fact which can be gathered by an examination of the above and other recipes (which will be given) for preparing the chrome-yellows. In consequence, the colour-maker can, by altering the proportions of the two bodies, produce almost any shade of yellow he may want. There is a direct connection between the quantities of the two bodies and that of the lead salt used; if the latter be kept constant, then, if the bichrome is increased, the quantity of Glauber’s salt must be decreased, and *vice versa*, so that no loss of material may result in making the chromes.

The following equivalents are given, so that the relative proportions of the two bodies may be kept correctly when the recipes are modified to produce other shades than those given above:—

1 lb. of Glauber’s salt is equal to 0·4 lb. of bichromate of potash.
 1 lb. of bichromate of potash is equal to 2·5 lbs. of Glauber’s salt.
 The difference between the values of acetate and nitrate of lead is so small that in practical use one may be considered equivalent to the other; and the same remark applies to the bichromates of

potash or soda. The above equivalents may be used in this way :—Suppose it is desired to make a yellow intermediate in shade between the lemon- and chrome-yellows given above, then $2\frac{1}{2}$ lbs. less bichromate must be used than for the chrome-yellow. The quantity of sulphate equivalent to $2\frac{1}{2}$ lbs. bichrome required to throw down all the lead is $2\frac{1}{2} \times 2\frac{1}{2} = 6\frac{1}{4}$; $6\frac{1}{4}$ lbs. of Glauber's salt must, therefore, be added to replace the $2\frac{1}{2}$ lbs. of bichrome taken away.

Cologne yellow is the name originally given to yellows containing lead chromate and sulphate, and made by precipitating with a mixture of potassium bichromate and sulphuric acid. Cologne yellows are generally made in two shades, pale and deep.

Pale Cologne Yellow.

Lead acetate,	100 lbs.
Potassium bichromate,	17 ,,
Sulphuric acid,	18 ,,

Deep Cologne Yellow.

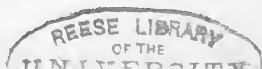
Lead acetate,	100 lbs.
Potassium bichromate,	25 ,,
Sulphuric acid,	13 ,,

They are made in the same way as the chrome-yellows above described, and are useful to mix with Prussian blue to make greens.

American Chrome-Yellow.—This is made by using alum in the place of Glauber's salt; the product is a fine one, the alumina salt seeming to have a beneficial influence on the fineness of the precipitate; still care is required in using alum, as otherwise there may be a difficulty in precipitating the pigments. The following recipes will give some idea of the proportions generally used :—

	Deep.	Medium.	Pale.
Lead acetate,	120	100	100
Potassium bichromate,	20	20	20
Alum,	100	100	100
Barytes,	40	60	80
Gypsum,	80

Another method of making chromes (which, however, is rarely used) is to take white lead, treat with nitric acid so that part



only of the white lead is dissolved, and then add bichromate of potash; according to the amount of white lead used in relation to the other constituents, so will the shade of yellow be; the following recipes may be taken as examples:—

For Chrome-Yellow.—Take 200 lbs. of white lead, mix with water to a fine paste, and then add 40 lbs. of nitric acid of 1.42 specific gravity (84° Tw.); when all effervescence has ceased more water is added, and then a solution of 35 lbs. of bichromate of potash; the yellow formed is finished in the usual way.

For a Deep Lemon-Chrome.—Take 300 lbs. of white lead, treat with water and 40 lbs. of nitric acid, as before, and precipitate with 35 lbs. of bichromate.

A cheaper class of chrome-yellows is made by precipitating the chromate of lead on to a white base; barytes, china clay, and whiting have been used for this purpose. When well made these are quite as good to use as the technically pure chromes described above, although the preference is given to the latter by most users.

The following recipes may be taken as standards for the preparation of these cheap chromes:—

Lemon Chrome-yellow.

Lead acetate or nitrate,	. . .	100 lbs.
Barytes,	. . .	400 „
Potassium bichromate,	. . .	35 „

Chrome-yellow.

Lead acetate or nitrate,	. . .	100 lbs.
Barytes,	. . .	200 „
Potassium bichromate,	. . .	35 „

Deep Chrome.

Lead acetate or nitrate,	. . .	100 lbs.
Barytes,	. . .	75 „
Potassium bichromate,	. . .	35 „

The depth of shade may be altered at will by varying the amount of barytes used: an increase in the amount reduces the depth of shade, while a reduction in the amount increases the depth; the quantities of the other materials need not be altered. The method of working has already been given.

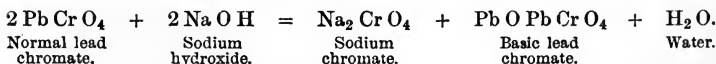
China clay can be used instead of barytes, and less weight of it will be required to produce any given shade than of barytes, owing to the china clay being so much lighter in specific gravity,

and, therefore, more bulky weight for weight, the relative power of the two bodies being as 1 to $2\frac{1}{2}$ or 3; that is, 1 lb. of china clay will tone down chrome as much as $2\frac{1}{2}$ or 3 lbs. of barytes. Gypsum may also be used, and is intermediate between china clay and barytes in its toning powers, but it is not so good for this purpose as the other two bodies, as there is a reaction between the gypsum and lead salts which renders it impossible to keep the lead in excess, and so there is a tendency to change the shade of yellow which is being made; when nitrate of lead is used instead of acetate this action of gypsum is more noticeable.

Whiting is sometimes used to tone down the yellows; for pale shades its use is not advisable, and, although it may be used for deep shades, yet the other whites just named are to be preferred. Being somewhat alkaline in its reactions and liable to contain traces of caustic lime, from being overheated in the process of manufacture, it often has an undesirable tendency to turn the shades of the yellows with which it may be mixed to an orange.

When barytes, china clay, gypsum, or whiting are used as toning colours it is advisable to grind them with water to ensure perfect admixture with the other ingredients of the yellow.

2nd. PREPARATION OF CHROME-ORANGES AND SCARLETS.—The affinity between the chromic acid on the one hand and of the lead on the other not being very strong, when the chromates of lead are treated with a stronger base, such as soda or potash, a part of the chromic acid is eliminated, and a basic chromate of lead is formed; this reaction is expressed by the following equation:—



The basic lead chromate has a deep red colour; if the action of the alkali only proceeds to a limited extent, then the basic red chromate formed combines with the excess of yellow normal chromate giving rise to an orange-coloured body, which is a mixture of the two chromates of lead; the shade of the orange pigment thus produced will depend, to a large extent, upon the amount of the action which takes place between the normal chromate and the alkali. The preparation of the chrome-oranges and scarlets depends upon the action of alkaline bodies upon the normal lead chromate. As with the yellows no actually chemically-pure oranges are made; the technically-pure colours contain more or less sulphate of lead, while the common colours generally contain barytes. The orange and scarlet chromes are much

easier to make than the yellows, as the conditions of making are more favourable to the production of orange shades than they are of the yellow shades. This is partly owing to the fact that these colours are made at a high temperature, while with the yellows it is necessary to keep the mass as cold as possible, if good yellows are to be obtained.

1. **Pure Chrome-orange.**—(a) 100 lbs. of lead acetate, 35 lbs. of bichromate of potash or soda, and 9 lbs. of caustic soda (77 per cent.*) are separately dissolved in water; the lead solution is run into the precipitating tank, the bichromate run in and chrome-yellow precipitated; this is allowed to settle, the clear top liquor run off and then the caustic liquor run on to the yellow; the mixture is heated until the desired shade is obtained; the orange is allowed to settle, the top liquor run off, and the colour washed with water two or three times, and when dried is ready for use. This recipe will give a pure chrome-orange.

(b) A cheaper method of making orange is as follows:—100 lbs. of lead acetate, 30 lbs. of bichromate of potash or soda, and 21 lbs. of Glauber's salt are used to make the chrome-yellow in the manner described above (p. 119). In another vessel 10 lbs. of quicklime are slaked to a thin cream; when ready this is strained through a sieve, so as to free it from any gritty particles, on to the chrome-yellow; the mass is now boiled (about an hour being generally required) until the colour has changed to an orange; the orange is finished as before.

The first of the above recipes will give a deep orange, the second a paler one; by varying the quantity of lead sulphate in the yellow, which is done by using more or less Glauber's salt, the shade of orange can be altered at will. The shade is also modified by the quantity of alkali used and the length of time the colour is boiled; the more alkali and the longer the boil the darker will the orange be.

2. **Common Chrome-orange.**—(a) *Pale Orange.*—Make a yellow as described above from lead acetate 100 lbs., barytes 200 lbs., and bichromate 35 lbs.; then add 10 lbs. of quicklime freshly slaked; boil till the shade has been developed, wash and dry the pigment.

(b) *Deep Chrome.*—Prepare a yellow from 100 lbs. of lead

* 77 per cent. caustic soda is nearly chemically pure; it is made by two firms in this country; if the more common and weaker makes of caustic are used, then a proportionately larger quantity of them must be taken; 10 lbs. of 77 per cent. soda are equal to $11\frac{1}{4}$ lbs. of 68 per cent. soda or to 13 lbs. of 60 per cent.

acetate, 75 lbs. of barytes, and 35 lbs. of bichromate ; then boil with 10 lbs. of freshly-slaked lime and finish as usual.

The shade of the orange is modified by the quantity of barytes, which may be used in proportion to the other constituents ; the amount of alkali used and the length of the boil also have some influence. Gypsum or china clay may be used instead of barytes if required.

3. **Pure Scarlet-chrome.**—(a) Dissolve 100 lbs. of lead salt, 35 lbs. of bichrome, and $12\frac{1}{2}$ lbs. of caustic soda (77 per cent.), each separately in water. Add the bichrome solution to the lead solution, allow the yellow precipitate to settle, run off the clear top liquor, then add the caustic solution and boil up the mixture, continuing the boil until the required scarlet shade has been fully developed ; then wash, dry, and finish the pigment in the usual way.

(b) 100 lbs. of white lead are mixed into a paste with water, 30 lbs. of bichromate of potash and $12\frac{1}{2}$ lbs. of caustic soda (77 per cent.) are dissolved in water, these two bodies being mixed together ; when ready the two solutions are mixed and boiled until the scarlet colour is developed ; the pigment is now finished in the usual way.

(c) See *chrome-red*, Runge's process.

3rd. **PREPARATION OF CHROME-RED.**—This body is also known as Persian red, Derby red, American vermilion, Chinese red, Victoria red, chrome-red, &c. It is the basic chromate of lead, PbO , $PbCrO_4$, whose composition and properties and principles of manufacture have already (p. 116) been dealt with.

Preparation of Chrome-red.—(a) To make this pigment 100 lbs. of white lead are mixed with water into a fine paste ; 50 lbs. of potassium bichromate and 15 lbs. of caustic soda (77 per cent.) are dissolved in water and mixed with the lead, and the whole boiled until the colour is properly developed ; the pigment is allowed to settle, the top liquor poured off, and the red washed, dried, and finished as usual.

(b) *Runge's Method.*—Runge has described the following method for preparing chrome-red:—448 lbs. of litharge are intimately mixed with 60 lbs. of salt (sodium chloride) and 50 gallons of water ; the mixture is allowed to stand for four or five days, stirring at intervals during that time, and adding water if the mass exhibits a tendency to set hard ; at the end of the time stated a semi-solid greyish mass will be obtained. 150 lbs. of bichromate of potash are now added, and the mass boiled for about two hours. The pigment formed is finished in

the usual way. This process has not given good results in the hands of the author; a scarlet-red is the deepest colour that could be got, which is too pale for chrome-red.

(c) *Prinval's Process*.—The best process which the author has tried for preparing chrome-red is that of Prinval, which is carried out thus:—Two equivalents (100 lbs.) of white lead, one equivalent of potassium chromate, K_2CrO_4 ($30\frac{1}{2}$ lbs. of potassium bichromate neutralised with caustic potash), and 50 gallons of water are mixed together and allowed to stand for two days; the mixture being stirred up at intervals. The mass is now boiled for half an hour or so until the red colour develops; it is allowed to settle, the top liquor run off, and the colour washed twice with water and once with weak sulphuric acid (4 lbs. in 40 gallons of water), then dried.

PROPERTIES OF THE LEAD CHROMES.—The chemical properties of these colours have been already (p. 116) described, so that it is only necessary here to deal with them so far as their properties as pigments are concerned.

The lead chromes are pigments of considerable brilliance of hue, and their covering power or body is very great, being superior to that of all other yellow colours, so that it is very difficult to find substitutes for them. The texture of these pigments is usually very fine, but there is considerable difference between the products of different makers in this respect. When well made they are very durable colours, exposure to all the ordinary atmospheric influences—heat, light, air, and moisture—having very little injurious action on them. Sulphuretted hydrogen and sulphur compounds turn them black, owing to the formation of the black sulphide of lead; some samples show a tendency to acquire a green hue when mixed with oil, which is due to an action between the chromic acid of the colour and the oil; probably in most cases when this occurs the action has been set up, in the first instance, by a small quantity of alkaline chromate left in the colour owing to defective washing, and this having a powerful action upon the oil oxidises it, and, at the same time, turns it green; this action having once been set up gradually extends throughout the mass of colour affected. This defect is more likely to happen with the oranges, scarlets, and reds than with the yellows.

The chromes are capable of being mixed with a large number of other pigments without being themselves affected or affecting others. It is not advisable to mix the chromes with pigments like ultramarine and cadmium yellow, which contain sulphur, as the mixture is apt to take a reddish tone owing to the formation

of a black sulphide of lead. Highly basic colours should not be mixed with chromes, as then they turn orange. Chrome-yellows do not work well with whiting in distemper work, as they sometimes turn orange; but the oranges and reds may be so used.

Chrome-yellow cannot be used along with lime or silicate of soda, or other alkaline vehicle, as these will turn them orange. The red seems to have a crystalline nature which it will lose by friction; in doing so, it turns of an orange colour; care must, therefore, be taken not to grind the red too much.

ASSAY AND ANALYSIS OF THE LEAD CHROMES.

—As there is such a great variation in the chrome colours, and one maker's lemon-chrome may differ from another maker's lemon-chrome, it is important to assay the chromes for colour, covering power, softness, and freedom from grit. The methods of assay will be found in Chapter X. Chrome-yellows are rarely adulterated, in a sense, as there is no cheaper yellow of an equal brilliance of colour; the only colour which could be used is yellow ochre, but such use is not practicable. An analysis of the chrome colours is rarely required; for a scheme for such an analysis reference may be made to the *Oil and Colourman's Journal* for September, 1888, or to the *Chemical News*, December 31, 1886. The following scheme of analysis, based on the one there given, gives satisfactory results:—

For Moisture.—Weigh out 2 grammes, dry in an air oven at 110° to 120° C. for a few hours, and, after allowing to cool, again weigh; the loss of weight shows the amount of moisture originally present.

For Lead.—Weigh out 2 grammes of the chrome, add 10 to 15 cc. of strong sulphuric acid, heat until the chrome is completely decomposed, allow to cool, dilute with water, add a little alcohol, filter, wash the precipitate well, mixing the first wash waters with the main filtrate, then dry, ignite, and weigh the precipitate or residue in a porcelain crucible. This residue, if the chrome be pure, consists of lead sulphate, $PbSO_4$; but if the chrome contain barytes or china clay, the residue will also contain those bodies. The amount of these, as ascertained by another operation, is deducted to find the weight of lead sulphate. This should be calculated to lead oxide by multiplying by 0.736.

For Chromium.—Boil the filtrate from the lead until all the alcohol has been driven off; then add ammonia in slight excess and boil well until the liquor is colourless; then filter, wash, dry, ignite, and weigh as usual. The residue on the filter is chromic oxide, Cr_2O_3 , and from its weight the quantity of lead chromate,

Pb Cr O_4 , in the chrome-yellow may be calculated by multiplying by 4.23. The amount of lead oxide corresponding to this can be calculated by multiplying by 2.9.

For Lead Sulphate and Barytes.—Weigh out 2 grammes, boil with strong hydrochloric acid until the chrome is completely decomposed; any insoluble residue is barytes or china clay; this can be filtered off, care being taken to filter while boiling and to wash the residue on the filter with boiling water, so as to prevent the precipitation of lead chloride from the solution. The residue, after drying, is weighed in the usual way. The filtrate from the barytes (or the solution in the acid, if there be no barytes) is boiled, and then barium chloride is added; the precipitate of barium sulphate is filtered while boiling and well washed with boiling water; it is dried, ignited, and weighed as usual. From its weight the amount of lead sulphate in the chrome may be calculated by multiplying by 1.3; and the amount of lead oxide corresponding to this by multiplying the lead sulphate by 0.736.

If the amount of lead oxide present in the form of chromate and sulphate does not equal that of the total lead oxide present, the difference may be considered to be present in the form of basic carbonate, and the amount of this can be calculated by multiplying by 1.16.

A qualitative analysis should, in all cases, precede the quantitative analysis, and the method of carrying this out modified accordingly. Should whiting be present, its amount may be ascertained by dissolving 2 grammes of the chrome in dilute nitric acid, filtering off any insoluble residue (which may be neglected), then precipitating the lead present as sulphate by adding sulphuric acid, and filtering the precipitate off, which may also be neglected. To the filtrate is added ammonia in slight excess (no precipitate should be obtained; if there be one, filter it off); then add ammonium oxalate, filter, wash, dry, and weigh the precipitate, the weight of which at once gives the amount of whiting in the chrome. If gypsum (calcium sulphate) be present, its amount may be ascertained by dissolving 2 grammes in hydrochloric acid, adding dilute sulphuric acid, allowing to cool, and filtering off any lead sulphate, lead chloride, and barytes which may be present; to the filtrate is added ammonia in slight excess (any precipitate which may be obtained is filtered off) and ammonium oxalate; the precipitate of calcium oxalate is filtered, washed, dried, and, after burning in a crucible, weighed; from the weight of calcium carbonate so obtained that of the calcium sulphate present may be calculated by multiplying by 1.36.

Schemes for the analysis of chromes based on the solution of

the lead chromate present in caustic potash have been devised, but the author does not consider that these give as satisfactory results as the scheme just described. The section on the analysis of Brunswick greens may be consulted.

ANALYSES OF "PURE" CHROME COLOURS.

CONSTITUENTS.	"Pure" Primrose Chrome.	"Pure" Pale Chrome	"Pure" Middle Chrome.	"Pure" Deep Chrome.	"Pure" Orange Chrome.	"Pure" Scarlet Chrome.	Chinese Red.
Water and volatile matter, }	6.900	2.48	1.850	5.640	3.625	1.275	1.69
Lead chromate, Pb Cr O ₄ , }	56.066	55.30	87.834	73.320	60.307	59.670	57.55
White lead, 2 Pb C O ₃ + Pb H ₂ O ₂ , }	.523	11.72	1.320	8.372	35.478	39.470	{ Pb O 39.99
Lead sulphate, PbS O ₄ , }	36.511	30.30	8.455	11.986
	100.000	99.80	99.456	99.328	100.410	100.415	99.03

ZINC CHROME.

This pigment is the chromate of zinc, Zn Cr O₄, which has the composition—

Zinc, Zn,	35.81 per cent.
Chromium, Cr,	28.93 "
Oxygen, O,	35.26 "
	<hr/> 100.00

or

Zinc Oxide, Zn O,	44.63 per cent.
Chromium trioxide, Cr O ₃ ,	55.37 "
	<hr/> 100.00

PREPARATION OF ZINC CHROME.—Zinc chrome is prepared in two ways—1st, by precipitating a solution of zinc sulphate with a solution of chromate of potash; 2nd, by treating zinc oxide with either chromic acid or potassium bichromate.

1st. **By Precipitation.**—The preparation of zinc chrome by precipitating solutions of zinc salts is very difficult, and only by the exercise of some care is the operation a success; this arises from the fact that zinc chromate is a substance which, while

insoluble in water, is readily soluble in acids and alkalies, and in various saline solutions. If the solutions used are slightly acid the zinc chromes will not form, consequently the acid bichromates cannot be used for preparing it. If the solutions are alkaline, then there is a tendency for the chrome to be decomposed, and for the white hydroxide of zinc to be formed.

The materials used in the preparation of zinc chrome are the sulphate of zinc and the chromate of potash; the chloride of zinc may be used or the chromate of soda. The principal points are the use of neutral solutions as strong as possible.

61½ lbs. of zinc sulphate are dissolved in as small a quantity of water as possible, and the solution is boiled; while boiling, a solution of 32½ lbs. of normal sodium chromate in water is added, and the mixture boiled for one hour; the zinc chrome is precipitated, and can be collected on a filter, washed, and dried at a low temperature. The solution of zinc should be neutral; as zinc sulphate is liable to be slightly acid the solution should be tested with a piece of paper dipped in a solution of Congo red, and if found to be acid, shown by the paper turning blue, then the solution should be neutralised by adding sufficient caustic soda. The solution of normal sodium chromate can be made by dissolving 26¼ lbs. of sodium bichromate in water, heating to the boil, and adding sufficient caustic soda to just neutralise the bichromate; this is best ascertained by the use of test paper made from a solution of phenolphthalein in methylated spirit, the caustic soda being added until a drop of the chromate solution taken out just turns the paper a faint pink. The solutions are now ready, and can be used as described above. The chrome so prepared is of a fine, deep, lemon-yellow colour, with a good body.

The reaction between the zinc and sodium salts is expressed in the equation:—



That with the potassium chromate is similar.

Another plan of making zinc chrome, and which gives good results, is to dissolve 61½ lbs. of zinc sulphate in water, and to add 26¼ lbs. of sodium bichromate dissolved in a small quantity of water; no precipitate will be obtained. The mixture is now boiled and, while boiling, a saturated solution of soda crystals is added in small quantities at a time, waiting between each addition until all effervescence has ceased; the addition is continued until there is little or no effervescence on adding more soda

crystals; the whole is now boiled for about one hour, during which period the zinc chrome will gradually precipitate, and may be filtered and finished in the usual way. Care must be taken not to add too much soda crystals or, otherwise, only a precipitate of zinc carbonate will be obtained. In both methods potassium chromate may be substituted for the sodium salt.

2nd. **From Zinc Oxide.**—This method was the subject of a patent taken out by *James Murdoch* in 1847, who describes the preparation of three shades of zinc chrome.

1. *A Marigold Tint.*—125 lbs. of bichromate of potash are dissolved in 70 gallons of water and boiled; 60 lbs. of zinc oxide are mixed into a thin cream with water and then poured into the bichrome solution; the mixture is allowed to stand for from 24 to 30 hours; after which it is boiled up for one hour, allowed to settle, and the colour finished as usual. The liquor from the colour is kept and used in making the second tint.

2. *A Lemon Tint.*—The liquor from the last tint, together with the first washings, are put into a boiler, and a solution of 75 lbs. of zinc oxide in 44 lbs. of sulphuric acid of $65\frac{1}{2}^{\circ}$ Tw. is added and the mixture is boiled for one hour; the colour formed is allowed to settle, the clear top liquor run off and kept for making the third tint, and the colour finished as before.

3. *A Pale Tint.*—The liquor from the second tint is now mixed with a solution of 15 lbs. of oxide of zinc in 7 lbs. of sulphuric acid, boiled and treated as before.

Clarke subsequently took out a patent in 1853, in which he describes the preparation of two shades of zinc chrome.

1. *A Dark Chrome.*—112 lbs. of bichromate of potash are dissolved in boiling water and 70 lbs. of zinc oxide, previously mixed with 35 gallons of water to a thin cream, added, and the mixture boiled for one hour; then the colour is allowed to settle, the top liquor poured off and used for making a paler tint (see below), and the chrome washed and finished.

2. *Lemon Zinc Chrome.*—The liquor from the deep chrome is boiled down till it has attained a strength of 26° Tw.; to every 8 gallons of this liquor 40 lbs. of zinc oxide, previously dissolved in 24 lbs. of sulphuric acid, are added; the mass is now boiled for one hour, the chrome allowed to settle, and, after decanting off the top liquor, washed and finished as usual.

Instead of potassium bichromate, chromic acid may be used with similar results. The following recipes may be used:—

1. *A Deep Chrome.*—Mix 100 lbs. of zinc oxide into a thin paste with 30 gallons of water; then add, by degrees, boiling the whole of the time, 130 lbs. of chromic acid; after the whole has

been added, continue the boiling for one hour longer; then allow the colour which has been made to settle, decant the top liquor and wash.

2. *Middle Chrome*.—Use 200 lbs. of zinc white and then proceed as above.

3. *Pale Chrome*.—Use 300 lbs. of zinc oxide, and proceed as above.

With all the processes just described there is great loss of chrome, as the liquors which are run off and the washings contain chromic acid, both free and in the form of chromates; these liquors are somewhat difficult to utilise; they might be used to make lead chromes, especially the oranges. This waste of chromic acid in making zinc chromes by these processes adds considerably to the cost. Another defect in the colours thus made is that they are very liable to be gritty, especially if the excess of chromic acid or alkaline chromate is not thoroughly washed out, for, if left in, this tends to crystallise in the colour; the presence of this chromate in the colour will lead to the colour, when mixed with oil, turning greenish, due to the oxidising action of the chromic acid on the oil.

The lead chrome plant shown in Fig. 18 may be used for making the zinc chromes.

PROPERTIES OF ZINC CHROME.—Zinc chrome is a yellow pigment of good colour and body; it is readily soluble in acids; all the common mineral acids dissolve it, even when dilute; it is also soluble in many organic acids. Caustic soda or potash, when mixed with it in small quantities, decompose it with the formation of zinc hydroxide and a chromate of the alkali; when in considerable excess they dissolve it. Ammonia will dissolve zinc chrome. Heat turns it a grey-violet tint, due to its decomposition into the oxides of zinc and chrome.

As a pigment it is quite permanent, resisting exposure to light and air when well made; while sulphureous gases do not affect the colour. It can be mixed with all other colours without being affected by them in any way.

Zinc chrome has usually a good colour and body, although in this respect it is scarcely equal to the lead chromes.

ASSAY AND ANALYSIS OF ZINC CHROMES.—In assaying zinc chromes the points to be noted are:—1st, colour; 2nd, covering power; 3rd, texture or freedom from grit, so as to have a soft feel; these points can be tested for in the usual way.

Zinc chromes are liable to adulteration with the lead chromes, as these are rather cheaper; or to form the pale shades the deep shades may be let down with a cheaper white base than zinc

oxide. Pure zinc chrome is soluble in acetic acid without effervescence; any yellow residue indicates adulteration with lead chrome or yellow ochre, which can be distinguished by the application of special tests. A white residue indicates adulteration with barytes, china clay, &c.; while admixture with either whiting or white lead will be indicated by effervescence with the acid. Zinc chrome should not be discoloured on adding to it a little ammonium sulphide.

A sample of zinc chrome analysed by the author had the composition:—

Water,	16·08 per cent.
Zinc chromate,	38·99 „
Zinc oxide,	4·93 „
	<hr/>
	100·00

LEMON CHROME. BARIUM CHROME.

This pigment is the chromate of barium, $Ba Cr O_4$, prepared by precipitating a solution of barium chloride with potassium bichromate. Its use as a pigment has become obsolete owing to its having only a very pale yellow colour and to its want of body. The lemon chromes made from lead are much brighter and have more body.

OCHRES AND SIENNAS.

Next to the chromes the ochres and siennas are by far the most important of the yellow pigments. They form a group of natural pigments of inorganic origin, found in comparatively large quantities in many parts of the world. The ochres are generally of a good yellow colour, varying from a faint brownish to a reddish tint of yellow; the siennas (which are so called because they were first found near the town of Sienna, in Italy) are of a brownish-yellow tint, varying somewhat in depth of shade.

Ochres occur in rocks of all geological ages; in the Oolitic rocks of Oxfordshire, the Mountain limestone of Derbyshire, the Silurian slates of Wales, the Granites of Cornwall, the Liassic and Cretaceous rocks of France, and in the volcanic rocks of Italy; so that geological age has no connection with their formation.

Ochres and siennas consist essentially of an earthy base, coloured, in the case of the ochres, by the hydrated ferric oxide; in the case of the siennas, by the hydrated ferric oxide and

manganese oxide. The character of the base varies according to the locality where the pigment is found. The analyses given below illustrate this point very well.

As stated above, these pigments owe their colour to hydrated peroxide of iron; so far as can be judged from the composition and manner in which they are found, this oxide of iron is, in all cases, an alteration-product, formed by the oxidation of ferruginous minerals, especially pyrites, and, in the case of siennas, of manganese ores. The manner of occurrence of ochres and siennas, so far as information at hand is available, appears to be different; in the case of ochres, these seem to have been formed by the decomposition and oxidation of iron minerals at the spot where the pigment is found, for, in the majority of cases, the ochre occurs more or less mixed with the gangue or matrix, from which mineral it originated. The analyses of the Welsh and Derbyshire crude ochres given below are examples of ochres formed in this manner. This occurrence of much matrix or gangue in crude ochres necessitates the adoption of a method of levigation to prepare them for use as pigments.

Siennas occur under various conditions, generally as aqueous deposits, in hollows and basins; some of these are of recent formation, since bronze idols and other articles of human manufacture have been found in them. Siennas seem to have been formed by water draining over beds of iron and manganese ores, so as to become charged with oxide of iron and organic matter, and then flowing into a hollow in which the iron, &c., it contained was deposited; in process of time the hollow was filled up and the bed of sienna formed. Siennas differ from ochres in containing very little extraneous matter, and, therefore, they require little beyond grinding to fit them for painting, when they are known as "raw sienna" (see p. 141).

Ochres are prepared for use as pigments by grinding and levigating. The plant used for this purpose varies at different works, its construction being largely dependent upon the nature of the ochre which is being treated. Some ochres are soft and powdery, these only require levigation; while others are harder, and need to be ground before they can be levigated. Fig. 28 shows one form of this plant, and in Fig. 12 is shown another form used in the china-clay industry, which may also be used for ochres. A is a large tank which, in Derbyshire and Cornwall, is known as the "buddle"; in this is placed the rough ochre, just as it comes from the ground, if the nature of the material permits; or it may be subjected to a preliminary grinding in an edge runner mill. In the buddle it is

thoroughly mixed with a constantly flowing gentle current of water, which carries off the finer particles of the ochre, and leaves the very coarse material behind; as the latter accumulates in the buddle it is removed from time to time and thrown away. From the buddle the water carries the ochre into a settling-tank, placed at a rather lower level, where the coarser particles of ochre settle out; when they have accumulated sufficiently the water is run out of the tank, and the ochre removed. From the first settling-tank the water, which still contains some ochre, is run into a second tank rather larger than the first, so that the current of water becomes more sluggish, and the finer particles of ochre subside more readily; in this second tank the ochre is allowed to settle until enough has accumulated, when it is removed as before. From the second tank the water runs off into a third tank, in which a still finer quality of ochre settles out. All these tanks are shown in Fig. 28; sometimes a fourth tank is arranged. The number of settling-tanks much depends upon the quality of crude material and the variety of grades of ochre it is desired to make; the grade of ochre which settles out in each tank is different from the others; that in the first is darker in tint and coarser in quality than that which settles out in the third; while, if a fourth tank is used, this will give a pale and fine quality of ochre. It will be found best in large works to arrange for three sets of settling-tanks, arranged side by side; the material from the buddle is run into the first of these sets until the tanks are full; then the stream is turned into the second set, which are also filled; then the stream is turned into the third set; by this time the ochre in the first set will have settled out, and the tanks can be emptied and got ready for the water to be turned into them. When the third set has become full the second set will be ready for emptying, and this is done; then the third set is emptied; thus there is always one set being filled, another settling out, and the third being emptied. There is scarcely two ochre works where the arrangement of the levigating plant is alike, as much depends upon the locality, the amount of water at disposal, and the quantity of material being treated.

After being taken out of the settling tanks the ochre is in the form of a paste which, as it contains probably 50 per cent. of water, must be dried. The arrangements for this vary very much at different works; at some, long horizontal flues are built with a fireplace at one end, and the flues covered with flagstones on which the wet ochre is placed; at others, the ochre is placed

in earthenware pans in an ordinary drying stove; but in every case, the drying of the ochre at as low a temperature as possible is important, as too high a temperature turns the colour of the ochre rather reddish.

PROPERTIES OF OCHRES AND SIENNAS.—So far as their properties as pigments are concerned, the ochres and siennas rank among the most permanent pigments at the disposal of the painter. They are unaffected by admixture with any other pigments, do not act injuriously upon other pigments, and are scarcely affected by exposure to the atmosphere and its destructive influences. They work well with all kinds of vehicles, and can, therefore, be used in any kind of painting—oil, water, distemper, fresco, &c.

Ochres and siennas vary very much in tint, brightness of colour, and strength. Oxford ochre is the brightest of the ochres and is of a fairly bright brownish-yellow colour. Siennas are of a brownish-yellow colour varying much in depth of tint or shade. Welsh ochres are rather duller than Oxford ochres; French ochres are moderately bright; Derbyshire ochres are reddish in tone and are darker than other varieties of ochre. They vary very much in texture; Oxford ochre and the siennas are of a soft texture; some are gritty in feel, while others have a clayey feel. In body or opacity these pigments vary much. The Oxford ochre and the siennas are rather transparent, and are commonly used as glazing colours; the other ochres are more opaque and have good body; hence, they are largely used as body colours, especially in house painting.

The colour of ochres is due to the presence of hydrated peroxide of iron, while siennas also contain small quantities of manganese; the shade or tint depends mainly upon the proportion of iron and manganese present, and also, but to a less extent, upon the degree of hydration of the oxide of iron; in proportion as the iron oxide is less and the hydration greater, the yellower and brighter the shade of colour; when the proportion of non-hydrated oxide of iron is large the shade becomes redder. When ochres are treated with hydrochloric acid, the iron they contain is nearly all dissolved out, and yields a yellow solution which will give the characteristic tests for iron, while a more or less insoluble residue is left behind.

Heat turns ochres a red colour, the shade of which depends upon the temperature and length of time the heating is carried on; these red colours are sold as Venetian red, light red, Indian red, &c.; their preparation and properties have already been described (see p. 105). Siennas are converted by heat into a

reddish-orange pigment, known as burnt sienna (see p. 141). This change of colour is due to the passage of the iron oxide from the hydrated to the anhydrous condition, but the reason why ochres should give reds and the siennas orange is not known.

ASSAY AND ANALYSIS OF OCHRES AND SIENNAS.—(a) **Crude Ochres and Siennas.**—These should be assayed for, first, the actual quantity of colour present and, second, for the tint or shade of the colour it gives. This last can be done in the usual way; the first can be ascertained as follows:—A tall glass of a conical shape is provided; a glass funnel with a long stem passes down to the bottom of the glass into which is put about 25 to 30 grammes of the crude ochre; into the glass is now passed a gentle current of water sufficiently strong to carry out of the glass all the finer particles of colour while leaving the heavier and more gritty particles behind, which are collected by filtering and, after drying, are weighed in the usual way; from the weight is calculated the proportion of colour and grit. Thus, the sample of crude Irish ochre (an analysis of which is given below) assayed in this way, was found to contain—

Grit,	30·24 per cent.
Colour,	69·76 ,,

(b) **Prepared Ochres.**—These only need assaying for colour and covering power by the usual methods.

It is rarely that an analysis of ochres and siennas is required; but analyses of several varieties are given below, which show their constituents and what to look for in analysing them. Ochres are rarely, if ever, adulterated. Ochres which are naturally poor in colour sometimes have a little chrome-yellow added to them to bring up the tint; such an addition may be recognised by treating the ochre with hydrochloric acid and alcohol, when a green-coloured solution containing chromium will be obtained, and the chromium in which may be detected by the usual tests.

COMPOSITION OF OCHRES AND SIENNAS.—Most of the following analyses have been made by the author; others are quoted from various published analyses. The notes appended to some of them will be found useful and of interest as showing some indications of the origin of these pigments.

1. **Oxford Ochre.**—The ochres from Oxfordshire have long had a reputation for their quality, exceeding, as they do, all other ochres in the brightness of their colour and depth of covering power. Most of the ochre is found in pits at Shotover, near

Oxford, of which the following section is given in "Ure's Dictionary":—

1. Summit of hill, highly ferruginous grit,	6 feet.
2. Grey sand,	3 "
3. Ferruginous concretions,	1 "
4. Yellow sand,	6 "
5. Cream-coloured loam,	4 "
6. Ochre,	6 inches.

Oxford ochre contains

Water, hygroscopic,	6·887 per cent.
Water, combined,	8·150 "
Calcium oxide, Ca O,	0·998 "
Sulphur trioxide, S O ₃ ,	1·321 "
Alumina, Al ₂ O ₃ ,	6·475 "
Ferric oxide, Fe ₂ O ₃ ,	12·812 "
Silica, Si O ₂ ,	63·478 "

100·121

The layer of ferruginous concretions is, probably, the source of the colouring matter of this ochre, while the clay which underlies the layer of ochre is the source of the base of the pigment.

2. **Welsh Crude Ochre.**—The exact locality from whence this sample was derived is not known; it has a fairly good colour and covering power. It contains

Water, hygroscopic,	2·000 per cent.
Water, combined,	12·500 "
Sulphur trioxide, S O ₃ ,	1·315 "
Silica, Si O ₂ ,	29·725 "
Alumina, Al ₂ O ₃ ,	33·315 "
Ferric oxide, Fe ₂ O ₃ ,	20·705 "
Copper sulphide, Cu S,	·515 "

100·075

Some of the iron oxide, 0·765 per cent., exists in a soluble form, probably as sulphate, for there is 0·555 per cent. of soluble sulphur trioxide. This, and the fact that there is copper sulphide present, indicate that this ochre has been formed by the decomposition of a cupreous pyrites, which supposition is further strengthened by the fact that small pieces of pyrites may be picked out of the crude ochre. This ochre requires well levigating to get rid of the pyrites as this body would introduce

an element of change which may exercise an injurious influence upon the permanent properties of the ochre.

3. **Irish Crude Ochre.**—This sample contains

Water, hygroscopic,	9·050 per cent.
Water, combined,	12·000 ”
Insoluble matter,	32·502 ”
Sulphur trioxide, $S O_3$,	2·685 ”
Alumina, $Al_2 O_3$,	16·770 ”
Ferric oxide, $Fe_2 O_3$,	26·381 ”
Calcium oxide, $Ca O$,	·258 ”
Copper oxide, $Cu O$,	·630 ”
	<hr/>
	100·260

The insoluble matter consists of silica and some gritty matter.

Of these constituents a portion (0·33 per cent. of sulphur trioxide, 0·191 of ferric oxide, 0·118 of calcium oxide, and 0·228 of copper oxide) was soluble in water in the form of sulphates, the iron being in the ferrous form; this points to the fact that this ochre was formed by the oxidation of the cupreous pyrites existing, disseminated through a siliceous mineral matrix which was broken up by the oxidation, and part of which went to form the base of the ochre, while much of it exists in the form of gritty angular pieces which must be separated before the ochre is fit to use as a pigment.

4. **Derbyshire Crude Ochre.**—This is of a reddish colour and is found incrusting masses of pyritous minerals and barytes, from which the ochre is separated by levigation. This ochre, like the others just noticed, has been formed by the oxidation of pyrites, small fragments of which, in an unchanged condition, are disseminated through the crude ochre. This sample contained more iron than any other examined by the author, as the following analysis shows:—

Water, hygroscopic,	5·400 per cent.
Water, combined,	6·000 ”
Alumina, $Al_2 O_3$,	1·040 ”
Ferric oxide, $Fe_2 O_3$,	76·081 ”
Calcium oxide, $Ca O$,	0·561 ”
Sulphur trioxide, $S O_3$,	1·744 ”
Pyrites, $Fe S$,	4·783 ”
Silica, $Si O_2$, }	4·394 ”
Barytes, $Ba S O_4$, }	
	<hr/>
	100·000

5. **Derbyshire Prepared Ochre.**—This sample is of a reddish

shade, not so dark as the last. The covering power of this ochre is good.

Water, combined,	6.100	per cent.
Barium sulphate, BaSO ₄ ,	20.946	„
Silica, SiO ₂ ,	4.530	„
Calcium sulphate, CaSO ₄ ,	2.516	„
Calcium carbonate, CaCO ₃ ,	21.755	„
Alumina, Al ₂ O ₃ ,	10.655	„
Ferric oxide, Fe ₂ O ₃ ,	33.498	„
Magnesia, MgO,	trace	
	<hr/>	
	100.000	

6. **Cornwall Prepared Ochre.**—This ochre is of a pale brownish-yellow shade and has not much covering power. It contains

Water, hygroscopic,	1.40	per cent.
Water, combined,	10.00	„
Silica, SiO ₂ ,	59.67	„
Alumina, Al ₂ O ₃ ,	9.72	„
Ferric oxide, Fe ₂ O ₃ ,	18.54	„
Calcium oxide, CaO,	0.23	„
	<hr/>	
	99.56	

7. **French Prepared Ochre.**—The exact locality from which this was obtained is not known to the author, but it is usually of a bright brownish-yellow colour with a good covering power.

Water, hygroscopic,	1.80	per cent.
Water, combined,	9.20	„
Silica, SiO ₂ ,	54.00	„
Alumina, Al ₂ O ₃ ,	13.75	„
Ferric oxide, Fe ₂ O ₃ ,	20.73	„
Calcium oxide, CaO,	0.19	„
	<hr/>	
	99.67	

8. **South Australian Ochres.**—The following analyses of South Australian ochres are quoted in the *Journ. Socy. Chem. Ind.*, 1889, p. 313:—

	Per cent.	Per cent.	Per cent.
Water, hygroscopic,	1.82	1.92	0.21
Water, combined,	6.48	7.60	4.00
Silica, SiO ₂ ,	41.20	56.60	65.20
Ferric oxide, Fe ₂ O ₃ ,	38.40	11.68	5.76
Alumina, Al ₂ O ₃ ,	12.56	19.12	21.74
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	100.46	96.92	96.91

9. **Siennas.**—The following are some analyses of raw siennas, which are of Italian origin—the first and second from the neighbourhood of Rome; the locality from whence the third came is unknown. The Roman siennas are found in hollows on hill sides, which hollows are now filled up with deposits of sienna; but, at one time, were the site of small ponds into which flowed streams highly charged with iron and manganese, from deposits of those materials situated above the ponds. The rocks of the district consist chiefly of trachyte and granite, charged with ferriferous and manganiferous minerals, which are the source of the colouring matter of the sienna.

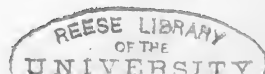
	Dark. Per cent.	Pale. Per cent.	Per cent.
Water, hygroscopic,	17·550	8·250	12·400
Water, combined and organic matter,	9·000	11·000	9·400
Silica, Si O ₂ ,	22·656	17·406	5·016
Calcium, carbonate, Ca C O ₃ , . .	0·960	1·075	4·460
Alumina, Al ₂ O ₃ ,	2·840	5·177	7·265
Manganese, Mn O ₂ ,	1·190	0·627	1·465
Ferric oxide, Fe ₂ O ₃ ,	45·820	57·032	59·965
Magnesia, Mg O,	trace.
	<hr/>	<hr/>	<hr/>
	100·016	100·567	99·701

It may be assumed that the shade of the siennas varies with the amount of manganese it contains, as is shown by the analyses given above.

The commercial value of an ochre depends upon its colour and body; those which excel in these points naturally commanding the best prices. The following is approximately the order of the various ochres as regards price:—Oxford, 100; French, 33; Derbyshire and Welsh, 25; Irish and Devon, 20.

BURNT SIENNA.

The siennas are sold in two forms, raw and burnt; the first has already been dealt with and the latter will now be described. Burnt sienna is prepared by calcining the raw sienna at a moderate red heat until it has acquired the desired shade. The tint of the burnt sienna depends not only upon the temperature used and the length of time it is exposed to heat, but, also, upon the shade of the raw sienna used. Burnt sienna is a pigment of a reddish-orange shade, very similar to that of the coal-tar colour known as Bismarck-brown. It is very transparent, and is, therefore, mostly used as a glazing or tinting colour by painters and



artists. It is sold in the form of small pieces, and of a paste ground up with water or oil. The former variety is very difficult to grind.

The composition of burnt sienna naturally resembles that of raw siennas, only that the heat has driven off most, if not all, the water the latter contains. The following analysis will serve to show the composition of burnt sienna :—

Water, hygroscopic,	9.450	per cent.
Water, combined,	3.275	”
Silica, Si O ₂ ,	36.912	”
Calcium carbonate, Ca C O ₃ ,	1.233	”
Manganese, Mn O ₂ ,	traces.	
Alumina, Al ₂ O ₃ ,	3.480	”
Ferric oxide, Fe ₂ O ₃ ,	45.650	”
	<hr/>	
	100.000	

The whole of the water in this sample had not been driven off by the burning. Why raw siennas should give an orange-red pigment on calcining and ochres a red is somewhat uncertain ; probably the fact that siennas contain organic matter and that the iron is in both the ferrous and ferric conditions may have some influence.

MARS COLOURS.

Under the generic name of Mars colours the late George Field, a noted colour manufacturer, introduced a series of yellows, oranges, reds, and violets, owing their colour to ferric oxide. Field did not publish any account of the method by which he produced these colours ; but descriptions of similar products have been given by various French and German writers on pigments. These colours present no advantage over ochres and iron-reds as regards permanency or brightness of tone, but have disadvantages as regards cost.

Mars yellow is made by taking equal weights of ferrous sulphate and alum, and adding a solution of carbonate of soda, thereby precipitating the iron and alumina ; the precipitate is collected, washed well with water, and dried slowly.

Mars orange is made by slightly calcining the yellow.

Mars red is made by calcining the yellow at a red heat.

Mars violet is made by calcining the yellow at a white heat.

By using milk of lime instead of the soda salt the colours could be made cheaper, a plan which is in use for making some forms of iron-reds (see p. 106).

Mars brown was made in a similar manner from a mixture of ferrous sulphate, alum, and manganese chloride.

Mars colours can be distinguished from the ochres and ochre-reds by being soluble in strong hydrochloric acid, and by containing a large proportion of alumina, but no silica.

TURNER'S YELLOW.

Turner's yellow (so named after the inventor, James Turner), or patent yellow (from its having been patented in 1781) was at one time largely used; but since the introduction of the chrome-yellows it has been gradually, and, perhaps, entirely abandoned. It has been known as Montpelier yellow, Cassel yellow, Kassler yellow, Verona yellow, mineral yellow, and, probably, by other names.

It is essentially an oxychloride or basic chloride of lead. It is made by mixing two parts of litharge and one part of salt with water to a thin paste and allowing the mixture to stand for 24 hours, stirring at intervals; at the end of this time it will, as a rule, have a white colour; if it has not, more water must be added and the mixture again allowed to stand for another 24 hours or until it becomes white; it is now washed (to free it from alkaline salts), dried, then put into a crucible, and calcined at a gentle heat sufficient to melt the mass. The shade of colour depends upon the temperature and duration of the heating; usually small samples are taken out of the crucible from time to time, and when the right shade has been obtained the contents of the crucible are allowed to cool, after which they are ready for use. Sal ammoniac may be used in the place of salt.

Another method of preparation consists in precipitating a solution of lead with hydrochloric acid, collecting the precipitate, and washing and calcining the lead chloride so obtained; but the result is not so good as that obtained by the process above described.

Turner's yellow is met with in many shades of yellow, from a fairly bright yellow to a dark orange-yellow; usually it is in the form of heavy, glassy-looking masses, which are rather difficult to grind. It has a good body or covering power, and can be used either as an oil- or water-colour. It is not a permanent colour, being affected by exposure to light and air and to sulphureous gases, which turn it brownish-black.

NAPLES YELLOW.

Like the last this is a lead colour and has been superseded by the chromes. Naples yellow is a compound of the oxides of

antimony and lead, and can be prepared of various shades and from different materials.

(a) 1 part of tartar emetic, 2 parts of lead nitrate, and 4 parts of salt are intimately mixed together, and the mixture placed in a crucible and heated to fusion, at which point it is kept for 2 hours; after which the fused mass is treated with water to wash out the soluble alkaline salts present in it, and the pigment is dried at a gentle heat.

(b) 1 part of tartar emetic, 2 parts of red lead, and 4 parts of salt are treated as above.

(c) 3 parts of antimony, 1 part of zinc oxide, and 2 parts of red lead are heated to fusion in a covered crucible for 4 hours; after which they are ground under water and the pigment dried at a gentle heat.

(d) A process of preparing an antimony-lead yellow from the dross of lead refining was patented in 1858, by *Dick*, which consisted in mixing this dross (which is a mixture of the oxides of lead and antimony with some small quantities of other impurities) with salt, fusing the mass for 2 to 3 hours, then washing it well with water and drying the pigment.

(e) A yellow not unlike Naples yellow has been made from the three oxides of tin, lead, and antimony, by calcining for 3 to 4 hours in a crucible a mixture of 2 parts of levigated crude antimony, 2 parts of tin ashes, and 5 parts of white lead; or 1 part each of tin ashes, litharge, and antimony may be used.

(f) 1 part of type-metal, 2 parts of potassium nitrate, and 4 parts of salt are fused together, and the fused mass treated as in process *a*.

(g) Processes for preparing antimony yellows were patented by *Hallet* and *Stenhouse*, in 1861, as follows:—1. Antimony ore was calcined and then mixed with oxide of zinc and litharge, the mixture being fused. 2. A mixture of type-metal and zinc oxide are fused together.

The yellows made by the above methods have been sold under various names—Naples yellow, Jaune, solid yellow, antimony yellow, &c. They were rather favourite colours at one time with artists, but their use has become nearly obsolete. They are bright colours, although not equal to the chromes in this respect; are fairly fast to light, but, like all lead colours, are affected by sulphureous gases; iron has an injurious effect upon these colours so that they cannot be ground in iron mills with safety. They are equally useful as oil- or water-colours, and are of good body or covering power.

KING'S YELLOW.

This yellow, which at one time was in extensive use, is the trisulphide of arsenic, As_2S_3 . It is found native as the mineral orpiment, which is sometimes ground up and used as a pigment. The artificial colour is usually made by precipitation, but it can also be made by sublimation.

1. *By Precipitation.*—(a) Arsenic is dissolved in hydrochloric acid and a current of sulphuretted hydrogen gas passed through the solution; a fine yellow precipitate of the colour is obtained, which is collected and dried at a gentle heat. (b) A fine yellow pigment, formerly sold under the name of Royal yellow, is made by mixing 2 parts of barium sulphate with 1 part of charcoal and calcining the mixture, when barium sulphide is formed; this is ground with orpiment and water into a fine paste, and by boiling with water a sulpho-arsenite of barium is obtained; to this is added dilute sulphuric acid which precipitates a mixture of barium sulphate and sulphide of arsenic as a fine yellow colour, which is collected, washed, and dried.

2. *By Sublimation.*—1 lb. of sublimed sulphur and 2 lbs. of white arsenic are thoroughly mixed together and placed in a crucible; this is covered with another crucible or with a special condenser, and heated in a furnace. The arsenic and sulphur react and form the sulphide, which, being volatile, sublimes into the cover, and is collected, washed, and dried; it varies a little from time to time in shade.

King's or arsenic yellow is a very bright pigment, almost rivalling the chromes in beauty. It has good body and works well either in oil or water, but is not a durable colour, as exposure to light causes it to fade, while air and moisture have no action on it. It does not mix well with other pigments, since, when associated with lead pigments, or with verdigris, emerald green, or other copper pigments, it gradually acquires a dark brownish tint owing to the formation of the black sulphides of lead and copper. It can be mixed with ultramarine, cadmium yellow, or oxide of iron without change. Being an arsenic colour it is very poisonous, and, therefore, its use is not to be recommended. Partly in consequence of this objection it has become nearly, if not entirely, obsolete. King's yellow forms a colourless solution with strong hydrochloric acid; as also with caustic soda, from which, on adding acid, the pigment is reprecipitated. The presence of arsenic may be tested for by means of Marsh's test, described in the section on emerald green (p. 171).

REALGAR, ARSENIC ORANGE.

Realgar is a native arsenic disulphide found in small quantities in various localities. It is prepared artificially by a process of sublimation as follows:—(a) A mixture of 8 lbs. of white arsenic (arsenious oxide) and 4 lbs. of flowers of sulphur are heated in a crucible as in making orpiment. (b) A mixture of 30 lbs. of arsenic, 20 lbs. of flowers of sulphur, and 40 lbs. of charcoal is made; a charge of 60 lbs. of this mixture is heated at a time in earthenware crucibles so arranged that the product which sublimes can be collected. This sublimate is then remelted to form the colour. Realgar has the same properties as orpiment.

INDIAN YELLOW.

Indian yellow or Purree is a most curious product. It has long been used in India, but is of comparatively recent introduction in this country, where its use is limited. It is made exclusively at Monghyr in Bengal by a caste of people known as the Gwalas. It is made from the urine of cows fed upon the leaves of the mango tree, which food increases the secretion of bile and the excess passes into the urine to which it imparts a strong yellow colour. The flow of the urine is stimulated by the Gwalas gently rubbing the urinary organs two or three times a day; indeed, the cows are so habituated to this that they are unable to pass the urine themselves; the feeding with mango leaves is so injurious that its long continuance causes the death of the cows, and grass, &c., is occasionally substituted for them; the average life of these cows is from six to seven years. The urine as it comes from the cows is collected, and each evening it is boiled down in earthen vessels when the yellow is deposited; it is gathered on calico, made into balls and sent into the market for sale. The annual production is said to be about 100 to 120 cwts.

Indian yellow is a fairly bright yellow pigment, and is sold in the form of small round balls; it is non-poisonous and has a good colouring power; unfortunately it is not durable, as exposure to light soon causes it to fade. Authorities differ somewhat upon the composition of Indian yellow, but most agree that it is a compound of a peculiar acid known as euxanthic acid (which exists in the purree) combined with magnesia; there is also present potassium benzoate and other bodies. The acid itself generally crystallises in small needles of a pale yellow colour; it is slightly soluble in cold water, more readily in boiling

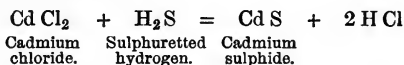
water, and freely in ether and alcohol. On being subjected to dry distillation a yellow body, called euxanthone, sublimes. The salts of euxanthic acid are all yellow-coloured bodies; those of the alkalies are soluble in water, while those of most of the metals are insoluble and may, therefore, be used as pigments.

CADMIUM YELLOW.

This important yellow pigment, so much used by artists on account of the brilliance of its colour and its permanence, is the sulphide of the metal cadmium and is composed of

Cadmium,	77·78 per cent.
Sulphur,	22·22 „

and has the formula Cd S. It is made by passing a current of sulphuretted hydrogen gas through solutions of cadmium salts, as shown in the equation:—



G. Buchner has investigated the properties of cadmium yellow more thoroughly than any other chemist. He describes* four modifications of cadmium sulphide which he distinguishes as

1. **A-modification**, obtained by passing a current of sulphuretted hydrogen gas through a slightly acid solution of a cadmium salt. The colour is a very bright and pure citron-yellow, has a good body, and works well as an oil-colour. By various means it can be converted into the B-modification. When used as an oil-colour it is quite permanent, but when used in water, or kept in a moist atmosphere, it gradually undergoes oxidation, passing into sulphate, this change being accompanied by a loss of colour.

2. **B-modification**.—This has a bright vermilion-red colour, and is obtained by passing sulphuretted hydrogen gas through a strongly acid solution of a cadmium salt. It is the most permanent form of cadmium sulphide and is unaffected by exposure to light and air.

The author has been unable to prepare this red variety of cadmium yellow. Although Buchner does not give any clear description of the method of obtaining it, yet from the remarks as to the conditions under which this red variety is formed, it is evident that it cannot be obtained by precipitation free from the yellow variety, and that the process of separation consists in

* *Chemiker Zeitung* quoted in *Journal Socy. Chem. Ind.*, VI. 665.

exposing the mixture of yellow and red sulphides to light and air for some considerable period. It is not practicable to prepare this variety as a commercial article.

3. **C-modification.**—A variety soluble in water, of no practical interest, and prepared by a process of dialysis.

4. **D-modification.**—This variety has a pale yellowish colour and little or no body. It is prepared by passing sulphuretted hydrogen gas through an ammoniacal solution of a cadmium salt. It is of no practical use.

Cadmium yellow is made commercially in various shades of yellow and orange, the processes for the production of which are described below.

Preparation of Yellow Cadmium.—This is prepared in several ways. 1. A slightly acid solution of any cadmium salt is prepared and through it is passed a current of sulphuretted hydrogen gas; the apparatus shown in Fig. 17, p. 111 may be used. This has a pure chrome-yellow shade. 2. A lemon-yellow shade is obtained by dissolving 1 lb. of cadmium sulphate in 4 gallons of water and adding $1\frac{1}{4}$ gallons of the ordinary yellow ammonium sulphide. 3. Or a solution of cadmium sulphate is made, to which is added a solution of sodium thiosulphate and a little sulphuric acid and the mixture boiled for an hour. This variety contains much free sulphur, and is, hence, liable to undergo oxidation to sulphuric acid, which destroys the yellow.

Preparation of Orange Cadmium.—1. A solution of cadmium sulphate or chloride is prepared. It is made strongly acid by the addition of excess of hydrochloric acid, and a current of sulphuretted hydrogen gas is passed through it. 2. 1 lb. of cadmium sulphate is dissolved in 4 gallons of water; the solution is boiled, and while boiling, yellow ammonium sulphide is added. All the precipitates of yellow obtained in the various ways just described must be well washed in water, especially those obtained with the ammonium sulphide, to free them from any trace of acid or sulphide which, if left in, would ultimately lead to the destruction of the colour. After being washed they should be thoroughly dried at as low a temperature as possible, not exceeding about 150° to 160° F.; too high a temperature causes the shade to become brown while hot and although the colour comes back on cooling, yet it never quite regains the original brilliancy.

PROPERTIES OF CADMIUM YELLOW.—Pure cadmium yellow is one of the most permanent pigments known; it is unaffected by exposure to light and air. It mixes with any vehicle used in painting. When heated strongly the colour darkens, changing to a dark violet-red; on cooling, the original

colour comes back, not, however, always in its original brilliance, but with a brownish tone. The impure yellows, those which are made with yellow ammonium sulphide or sodium thiosulphate, are not permanent pigments. When they are exposed to the combined action of air and moisture, the free sulphur they contain becomes oxidised to sulphuric acid, and this, acting on the yellow cadmium, changes it to sulphate, which change is shown by a bleaching of the colour, and occurs whether the pigment be ground or used in oil or water.

Cadmium yellow can be mixed with almost all the other pigments without affecting them or being affected by them; the only exceptions are those pigments which, like white lead, emerald-green, and the chrome-yellows, contain lead or copper as their basis. When such pigments are mixed with cadmium yellow double decomposition sets in, resulting in the formation of black sulphide of lead or copper as the case may be; the production of either compounds causes the mixture to acquire a greyish or brownish tint.

ASSAY AND ANALYSIS OF CADMIUM YELLOW.

—Besides the usual tests for colour and body, cadmium yellow should satisfy the following tests:—Strong hydrochloric acid should completely dissolve the yellow with evolution of sulphuretted hydrogen to a clear colourless solution, from which, on dilution with water and passing sulphuretted hydrogen gas, a yellow precipitate only should be obtained. The filtrate from this precipitate should give no precipitates on adding ammonia and ammonium sulphide. The addition of barium chloride to the solution should produce no turbidity. On boiling with caustic soda, filtering off the residue and adding hydrochloric acid to the filtrate no yellow precipitate, indicating the presence of arsenic yellow, should be obtained. Carbon bisulphide should extract no sulphur from it. Samples should not yield anything to water when boiled with it. The aqueous liquor should not give any precipitates with silver nitrate or barium chloride nor any acid or alkaline reactions to test papers.

Cadmium yellow is rarely adulterated; the common adulterants are arsenic yellow, zinc chrome, and the chrome-yellows, the presence of which can be distinguished by the application of the characteristic tests, which are given under the respective pigments.

AUREOLIN.

This pigment is a double nitrite of potassium and cobalt prepared by precipitating cobalt nitrate with sodium carbonate,

dissolving the precipitate in acetic acid and adding a strong solution of potassium nitrite. On allowing the mixture to stand for some time the colour is gradually precipitated, and is collected and washed; after being dried it is ready for use.

Aureolin is of a bright yellow colour, but is not permanent, being affected by exposure to light and air; acids dissolve it, while alkalies have no action.

CHAPTER V.

GREEN PIGMENTS.

THE green pigments in common use by the painter and the artist are derived from both natural and artificial sources, but usually from the latter. The green pigments are valuable, largely made and used, and are fairly numerous.

The commonest are those known as Brunswick greens, which are made in very large quantities for common painting; next is emerald-green, although this colour, owing to its poisonous nature, is gradually being displaced by substitutes made from the coal-tar greens; then comes the true chrome-green; then some of the other copper-greens; while the rest are only used on a limited scale.

BRUNSWICK GREEN.

Under the names of "pale Brunswick green," "middle Brunswick green," "deep Brunswick green," are sent out several green pigments, varying in shade or tint from a pale yellowish-green to a very deep blue-green. These pigments are made in very large quantities, and are mixtures, in various proportions, of chrome-yellow, Prussian blue, and barytes. They must not be confounded with the pigment originally known under the same name, which was a compound of copper, and which has almost completely gone out of use.

Brunswick greens can be made in various ways, almost every colour maker having his own favourite manner of mixing the various ingredients together.

DRY METHOD.—In this method the materials composing the green are thrown into the pan of an edge-runner grinding mill or into a mixing mill; the former is preferable, as the materials are ground as well as mixed, and this has some influence in developing the tint of the green. The main advantage in this method is considered to be that the shade of green which is being produced is visible while in the mill, and that if too

much yellowing is being produced as compared with a standard sample, then, by throwing a little more blue into the mill, the fault can be remedied at once; but against this advantage must be set off the disadvantage that the tints of green are not so fine as those which are obtainable by wet methods. The following proportions can be taken as guides in making the various shades of Brunswick green by this dry method:—

Pale Brunswick Green.—1 cwt. of barytes, $1\frac{1}{2}$ lbs. of Prussian blue, and 35 lbs. of chrome-yellow.

Middle Brunswick Green.—1 cwt. of barytes, $2\frac{1}{2}$ lbs. of Prussian blue, and 35 lbs. of chrome-yellow.

Deep Brunswick Green.—1 cwt. of barytes, 5 lbs. of Prussian blue, and 35 lbs. of chrome-yellow.

Extra Deep Brunswick Green.—1 cwt. of barytes, 8 lbs. of Prussian blue, and 35 lbs. of chrome-yellow.

The quality and tint of the chrome-yellow used will be found to have some influence upon the tint of the green produced; for the pale shades lemon-chromes should be used; while for the deep shades the middle shades of chrome can be used. Before making up a large batch of green with a new batch of either chrome-yellow or Prussian blue a small trial lot should be made to see if the two pigments will produce the required shade, as experience shows that different makes of chrome-yellows, even if of the same shade, do not always give the same results in making these greens; while the difference between two makes of Prussian blue as green-producers is greater than that between two makes of chrome-yellow.

For making the palest shades of Brunswick greens, only the best and brightest Prussian blues should be used; for the darker shades of green the quality of the blue is not of so much consequence.

The barytes may be replaced with gypsum, if thought fit; less gypsum is required to produce a given tint of green than barytes, the proportion being about 1 cwt. of gypsum to $2\frac{1}{4}$ cwts. of barytes.

WET METHODS.—The wet methods are those commonly adopted by makers of Brunswick greens, partly because they are the oldest (for colour makers are so conservative that it is difficult to induce them to alter their methods), and, partly, because the wet methods produce the finest greens; but they are very much more troublesome to carry out and require no little practical experience on the part of a colour maker to produce the best results. From the recipes which have been given above it will be seen that barytes is the principal ingredient in these greens; hence the principle which should underlie all wet pro-

cesses is to precipitate the yellow and the blue constituents on the barytes simultaneously. This is by no means easy to do, and yet much of the brilliancy of the green depends upon this being done as successfully as possible. The best way to ensure this result would be to mix solutions of the acetates of lead and iron or of the nitrates of those metals together and to add the barytes and precipitate with a mixture of the bichromate and ferrocyanide of potash, but, unfortunately, this course is not at present available, for the reason that while the acetate or nitrate of lead can be purchased on a commercial scale of sufficient purity, the acetate or nitrate of iron is not so purchasable; the common iron liquor is too impure for use in making greens, while the nitrate of iron so-called is of too variable a composition to be recommended for use in colour making.

The materials which are used in the preparation of the greens are copperas (ferrous sulphate), which should be used as pure and as fresh as possible, the variety known as green copperas is the one required, acetate of lead, bichromate of potash, ferrocyanide of potassium (yellow prussiate of potash), and barytes. The red prussiate of potash would give rather better results than the yellow, only that its extra cost is against its use for making greens for common use; but when a good price is obtainable its use is to be recommended, as the green is much easier to make with it than with the yellow prussiate.

For producing the various shades of Brunswick greens the following proportions may be used which, as well as those given above, may be varied so as to suit the special requirements of each individual maker. The following points are, however, well worth attending to in making alterations in the proportions. 1st. That equal weights of prussiate and copperas must be used. 2nd. That the proportion of acetate of lead to the bichromate of potash should be, as nearly as possible, 10 to 3½.

Pale Brunswick Green.—1 cwt. of barytes, 13 lbs. of acetate of lead, 1 lb. of copperas, 1 lb. of yellow prussiate of potash, and 4 lbs. of bichromate of potash.

Middle Brunswick Green.—1 cwt. of barytes, 13½ lbs. of acetate of lead, 1½ lbs. of copperas, 1½ lbs. of yellow prussiate of potash, and 4¼ lbs. of bichromate of potash.

Deep Brunswick Green.—1 cwt. of barytes, 14 lbs. of acetate of lead, 2 lbs. of copperas, 2 lbs. of yellow prussiate of potash, and 4½ lbs. of bichromate of potash.

Extra Deep Brunswick Green.—1 cwt. of barytes, 16 lbs. of acetate of lead, 4 lbs. of copperas, 4 lbs. of yellow prussiate of potash, and 5 lbs. of bichromate of potash.

Instead of the bichromate of potash the bichromate of soda may be used with some advantage, on account of its greater solubility and less cost.

Instead of barytes, any white pigment may be used, when it will be found that a smaller quantity will be required to give a green of the same depth of colour; or, to put it in another way, an equal weight of another white base will require a greater quantity of the other ingredients to produce the same shade of colour; with gypsum the proportion will be about $2\frac{1}{2}$ times as much, with china clay about 3 or 4 times as much, and with zinc white from 4 to 5 times as much; it is very rarely that any other pigment than barytes is used in making these greens.

By varying the proportions a great variety of green shades can be produced. It is mainly owing to the variable proportions used that the middle green, say, of one maker so seldom has exactly the same tint or depth of colour as that of another maker.

The following is the best method of working, in order to obtain good bright pigments with the ingredients given above. The iron salt is dissolved in a tank of cold water, the lead salt is similarly dissolved in another tank, while the two potash salts can be dissolved together in one tank. The barytes is thoroughly mixed with water in another tank, and, when properly mixed, the iron solution is run in with constant stirring; and then the lead salt is run in. Some of the lead will be precipitated as the sulphate, owing to double decomposition taking place between the two salts, but this cannot be avoided, so that allowance should be made for it in all recipes for making Brunswick green by increasing the amount of acetate of lead as the quantity of copperas is increased; every extra pound of the latter will require 1 lb. 3 oz. of acetate of lead to be added in addition to that required to form chrome-yellow with the bichromate. After the lead has been run in and mixed with the rest of the ingredients, the whole is kept stirred while the potash salts are run in; the green soon forms and is allowed to settle; the clear liquor at the top is run off and the pigment washed by running in water and stirring well, again allowing to settle and running off the wash waters; this washing should be repeated once or twice. Then the colour is taken out, thrown on filters to drain, and, finally, dried at a gentle heat. Various other methods of manipulating the preparations of these greens are in use among the various makers, but it is not necessary to describe them.

A method of working, which has been used by the author with very good results as to ease and quality of the colour produced,

is to grind all the ingredients together, in the proportions given above, in an edge-runner mill, and when they are properly mixed, to put them into the tub and run water on to them, with constant stirring; the green is rapidly developed, and is allowed to settle; the clear top liquor is then run off, and fresh water run on to wash the pigment, after which it is finished as usual.

These greens are sold under a variety of names—Brunswick green (which is the commonest), Chrome-green, Victoria green, Prussian green, &c.

COMPOSITION AND PROPERTIES OF BRUNSWICK GREENS.

These pigments are compounds of barytes, chrome-yellow, Prussian blues, with occasionally small quantities of lead sulphate, gypsum, and other bodies. The following analyses made by the author of different shades of these greens, of a good make, will show the average composition of the pigments:—

ANALYSES OF BRUNSWICK GREENS.

	Pale.	Middle.	Deep.	Extra deep.
Water,	1·000	0·800	1·000	0·800
Barytes,	72·744	71·944	72·764	71·404
Gypsum,	2·341	traces.	traces.	...
Prussian blue,	0·929	0·442	4·543	6·910
Chrome-yellow,	14·266	25·734	17·660	17·867
Lead sulphate,	8·073	1·039	3·280	3·152
	99·353	99·959	99·247	100·130

They are good pigments, and work well both in oil and water, especially the former; their opacity is good, and, therefore, they have good body or covering power, in this respect surpassing all other green pigments. They can be mixed with other pigments, with but few exceptions, without any change being brought about by interaction; these exceptions being those pigments containing sulphur, which would act upon the chrome-yellow and darken the green, by the production of black lead sulphide and highly basic colours, like whiting or lime, which would act

both upon the chrome-yellow and the blue, turning the green into a red.

They are fairly permanent when exposed to light and air, for, although not quite permanent, they are so for all practical purposes; exposure to light causes the yellow constituent to fade first, as a rule, so that, especially in the dark shades, the green has a tendency to turn blue, but in this respect the blue is very variable; in some makes the yellow goes first, in others the blue, much probably depends upon the composition of the particular green and the circumstances under which it is placed.

Acids turn the colour bluer, owing to their dissolving out the chrome-yellow; on the other hand, alkalies turn it orange, owing to their combined action both on the blue (turning this of a reddish-brown) and on the yellow (which they turn orange), as is noted in describing the blue and the yellow in their respective places. Sulphuretted hydrogen darkens the tint considerably.

ASSAY AND ANALYSIS OF BRUNSWICK GREENS.

—Brunswick greens require assaying for colour or tint, covering power or body, brilliance, &c., by the usual methods. Since, as already stated, the pale shade of one maker may not exactly agree with the pale shade of another maker, the different makes should always be compared together for the various properties just named; as a rule, it will be found that different batches of the same maker's green will match one another very closely.

It is rarely that an analysis of these greens is required; but, if so, the following method, described by Brown,* may be followed:—

1. For **Chrome Green**.—Weigh out 2 grammes of the green, treat with 28 to 30 cc. of strong hydrochloric acid, at the boil, for about 10 minutes, then filter while still hot, and wash well with boiling water, adding the wash waters to the filtrate.

The residue, consisting of barytes and Prussian blue, is strongly heated until the blue is decomposed, and, after cooling, the residue is weighed; this gives the weight of oxide of iron and barytes in the green. Treat the residue with a mixture of nitric and hydrochloric acids, boil well, then dilute with water and filter; dry, ignite, and weigh the residue, which is the barytes; deduct this weight from the original weight of barytes plus oxide of iron; the difference is the amount of oxide of iron, which, multiplied by 2.212, gives the amount of Prussian blue in the green.

Filtrate.—Nearly neutralise by the addition of ammonia, then

* Brown, *Chemical News*, December 31, 1886.

pass a current of sulphuretted hydrogen gas through the solution, which will precipitate the lead as lead sulphide; filter this off and wash the precipitate, adding the wash water to the filtrate.

Lead Sulphide.—Treat the precipitate of lead sulphide with hot nitric acid, boil down to a small bulk, then add a little strong sulphuric acid, heat until acid fumes begin to appear, then allow to cool, add water and a little alcohol, filter, wash, and, after drying and igniting the precipitate in the usual way, weigh as lead sulphate. This gives the total amount of lead in the green, which may be in the condition of sulphate as well as of chromate (see the analyses given above).

Filtrate from the Lead Sulphide.—This contains the chromium and occasionally a little iron. Boil down to a small bulk, then test the solution for iron by taking a drop out with a glass rod and placing it on a piece of paper moistened with potassium ferrocyanide; if a blue spot appears, then iron is present, and the solution is treated according to method No. 1; if iron is absent it is treated according to method No. 2.

Method No. 1.—Boil the solution with nitric acid and potassium chlorate until a clear yellow solution is obtained, then add sufficient ammonia to precipitate the iron, filter off, wash, dry, and weigh the precipitate, which weight is to be added to the weight of the iron previously found. Take the filtrate from the iron precipitate, boil down to a small bulk, add some strong hydrochloric acid and a little alcohol and boil until the colour of the solution becomes a clear green; this is effected by cautious addition of more acid and alcohol, if required, but too great excess of either must be avoided; to the solution is added ammonia in excess and the mixture is boiled until it gives on filtering a colourless filtrate; the precipitate consists of chromium hydroxide, which is filtered off, dried, ignited, and weighed; the weight multiplied by 4.241 gives the weight of chrome-yellow (pure chromate of lead) in the green.

Method No. 2.—The filtrate from the lead sulphide in which no iron is present is boiled and ammonia added in excess; the mixture is then treated as described under method No. 1, from the same point.

2. For **Lead Sulphate.**—Weigh out 2 grammes of the green, boil with hydrochloric acid, filter while still hot, and wash with boiling water; evaporate the filtrate down and, while still boiling, add barium chloride in slight excess; filter, wash well with boiling water, and treat the precipitate of barium sulphate in the usual way. The weight of barium sulphate multiplied by 1.3 gives the weight of lead sulphate in the green. The difference

between this amount and that found in the first instance represents the lead which is present in the green in other forms.

A qualitative analysis should always precede a quantitative one; and the above scheme should be modified if such an analysis shows that other constituents, besides those mentioned above, are present in the greens. The notes on the analysis of chrome-yellows (p. 127) will be found useful.

BRUNSWICK GREEN.

The modern Brunswick greens must not be confused with the pigment which was made and sold at one time under this name and which has now become quite obsolete. This old Brunswick green was a basic chloride of copper, sometimes called an oxychloride, $\text{Cu}_2\text{O Cl}_2$. It can be prepared by several methods.

1. 20 lbs. of copper turnings are placed in a vessel capable of being closed; over them is poured a solution of 30 lbs. of ammonium chloride in 6 gallons of water; the vessel is closed up and the contents well mixed by shaking; the vessel is kept in a warm place for about two months, and at intervals the contents are mixed by shaking up; at the end of the time the vessel is opened, when it will be found that most of the copper has been converted into the green oxychloride.

2. Into a wooden tub is placed about 1 cwt. of old sheet copper cut into small pieces; over them is poured a solution of 105 lbs. of sulphate of potash and 1 cwt. of common salt; the mass is allowed to react together for some time, the length of which depends upon the temperature, and is longer in winter than in summer. The green gradually forms, and when it is seen that most of the copper has been converted, the green is separated from the undecomposed copper by sieving and washing.

3. 1 cwt. of copper is mixed with 67 lbs. of salt and 34 lbs. of sulphuric acid mixed with 3 times its volume of water; after standing some time the green is formed, when it is treated as before.

4. Metallic copper is taken and just covered with a strong solution of chloride of copper and left until it is changed into the basic chloride, when it is finished as described under method 2.

The preparation of Brunswick green is a very slow operation, extending over 2 to 4 months as a rule; in all cases the green is collected by washing it with water to free it from any alkaline bodies, sieving to free it from unchanged copper, drying slowly at a low temperature, since high temperatures tend to decompose it; necessarily it is somewhat costly.

As a pigment it is fairly good, working well both in oil and water, and having a good covering power; in tint it has somewhat of a bluish-green cast of no great depth of colour. It is not quite permanent, although it resists some considerable amount of exposure to light and air. In its general properties it closely resembles the Bremen blues and the Bremen greens, which see.

CHROME-GREEN.

True chrome-green is a most valuable pigment, not only on account of the brilliance of its colour, but also on account of its great permanence, being in fact the most permanent green pigment known.

In its chemical composition chrome-green varies somewhat according to the method of making; in some cases it consists entirely of the oxide of chrome, Cr_2O_3 ; in others of the phosphate of chrome, $\text{Cr}_2\text{P O}_4$; while in yet others it is a mixture of these bodies. It should not be confused with the mixture of chrome-yellow and Prussian blue which is sometimes sold as chrome-green.

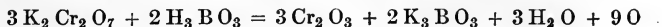
Various methods are in use for preparing chrome-green.

1. *Guignet's Process*.—Guignet was one of the first to prepare chrome-green, if not the very first; hence the pigment is frequently sold under the name of "Guignet's green." Guignet uses boric acid (boracic acid) and bichromate of potash. As a rule, the commercial articles are of sufficient purity to prepare good pigments with. But if very good results are required it is advisable to purify them by re-crystallisation.

88 lbs. of potassium bichromate and 33 lbs. of boracic acid are ground into a stiff paste with water; the mixture is then put into a furnace where it is heated to a dark red heat for 4 hours. A form of reverberatory furnace is the best that can be used. The fused mass is thrown into water and repeatedly washed by decantation; the washed pigment is ground whilst still wet under an edge-runner mill, again washed, filtered, and dried.

The first wash-waters contain a good deal of the boracic acid in the form of potassium borate; this acid may be recovered and used over again; the waters are boiled down a little and to the liquor is added hydrochloric acid; this throws out the boracic acid, which gradually collects in the form of crystals on standing; these crystals can be collected and used for making another batch of green; in this way at least 70 to 75 per cent. of the boracic acid originally used is recovered.

The reaction which takes place between the boracic acid and the bichromate is expressed in the following equation:—



from which it can be calculated that a considerable excess of boracic acid has been used in the process of making the colour; this excess is not wasted, since part is recovered, and, moreover, an excess is necessary for the production of a fine quality of the pigment. Borax cannot be substituted for the boracic acid.

Chrome-green made by this process has a fine yellow-green tint.

2. 3 lbs. of bichromate of potash and 2 lbs. of ammonium chloride are thoroughly mixed together into a paste with water; this is dried and then calcined at a red heat in a furnace; the calcined mass is well washed in water, and the pigment thus obtained is ground. This process gives a fine quality of green, but it is not quite equal to that obtained by the last process.

3. When solutions of ammonia or caustic soda or carbonate of soda are added to solutions of the basic chromium salts a precipitate of the hydroxide, $\text{Cr}_2 \text{H}_6 \text{O}_6$, is obtained; when this is heated to redness it loses water and passes into the oxide, $\text{Cr}_2 \text{O}_3$; the tint of green obtained in this way is not good, being of a greyish hue; by mixing with the precipitate some salt before calcining, and afterwards thoroughly washing with water, the tint of the green is materially improved.

All the above processes yield the green in the form of oxide, $\text{Cr}_2 \text{O}_3$, which is perfectly permanent when used as a pigment.

4. A solution of chromium chloride is prepared by heating a strong solution of potassium bichromate with hydrochloric acid and a little methylated spirit; to this solution is added, first, sufficient soda to neutralise the acid, and, then, a solution of sodium phosphate; the precipitate of chromium phosphate is collected, dried, and calcined; the green is then finished by washing and grinding in the usual way.

5. A cheaper method of producing the phosphate consists in preparing a solution of 10 lbs. of potassium bichromate and 18 lbs. of sodium phosphate; the mixture is boiled, and, while boiling, a solution of 10 lbs. of sodium thiosulphate is added, and then a little hydrochloric acid. On continuing the boiling the chromium phosphate is slowly precipitated; when the precipitation is complete, the green is treated as in the last process. The pigment obtained by this process is apt to contain a trace of sulphur, which introduces into it an element of change.

The phosphate-of-chrome greens are by no means equal to the oxide-of-chrome greens for brilliancy of tint.

PROPERTIES OF CHROME-GREEN.—Chrome-green forms a fine green pigment of a slightly yellowish tone; it mixes well with either oil or water, has good body or covering power, and is quite permanent, being one of the best pigments which the painter can use, on which account it is much used by artists. It mixes with all other pigments without being affected by them or altering them in any way.

When properly made it is quite insoluble in either acids or alkalis. The solubility of oxide of chromium depends upon the temperature and length of time to which it has been heated; the greater these two factors are the more insoluble becomes the oxide, so that well prepared oxides are very insoluble owing to the fact that they have to be heated to a high temperature for some time.

Very nearly the same property is found in the phosphate greens.

ASSAY AND ANALYSIS OF CHROME-GREENS.—Chrome-greens should be assayed for colour, brilliance, covering power, and similar properties in the usual way. When pure, chrome-green should not impart a yellow colour to dilute hydrochloric acid when boiled with that reagent, such yellow colour would indicate adulteration with chrome-yellow. When boiled with caustic soda chrome-green should remain unacted upon. The liquor should be divided into two portions—to the one acetic acid should be added, when no yellow precipitate indicating chrome-yellow should be obtained; to the other hydrochloric acid and ferric chloride should be added, when no blue precipitate should be obtained, such precipitate would indicate the presence of Prussian blue. Chrome-greens are usually adulterated with the Brunswick greens, which adulteration is detected by the application of the two tests just given. For use by calico-printers, Guignet's green is supplied in the form of a paste, containing usually 30 per cent. of actual colour.

COPPER GREENS.

Copper forms the base of a number of greens, some of which are of value, although the bulk are of but minor importance, and their use is gradually decreasing. The variety of names under which the copper-greens have been offered from time to time is very great; very few are now in use, and it is rather difficult to know exactly to what copper compound any particular name one meets with in old books and papers belongs. One of these greens has already been described.

Three of these copper-greens—verdigris, Scheele's green, and emerald green—are very closely related to one another, and form, as it were, a group of colours. Verdigris is the basic acetate of copper. Scheele's green is the arseniate of copper, while emerald green is the aceto-arsenite of copper, and may be viewed as a compound of the other two colours.

VERDIGRIS.

The chemical composition of verdigris has been already stated. It is made in two forms, known as "distilled" and "common" verdigris. The first, being somewhat of a crystalline nature, is rarely used as a pigment, and finds its chief use in medicine; the latter is of the most importance from a painter's point of view.

Preparation of Verdigris.—Distilled verdigris is prepared by dissolving copper or oxide of copper in the acid obtained during the distillation of wood, from which circumstance arises the name "distilled verdigris;" for the product itself is not distilled. Another method of manufacturing this variety is to mix together solutions of sulphate of copper and acetate of lime, or of the acetate of lead; the sulphate of lime or lead, as the case may be, is precipitated, and a solution of acetate of copper is obtained. From the solution of acetate of copper, obtained by either of the above methods, the verdigris is obtained by concentrating down to the crystallising point, and allowing the salt to crystallise out; this gives the best product. Or, the solution may be cautiously evaporated to dryness; this is costly and there is a risk of decomposing the green, causing it to lose its brilliancy of tint.

Distilled verdigris occurs in the form of dark green crystals, soluble in water and in acetic acid; as a pigment it is of little use, being too transparent; then, again, its solubility is against its being a good pigment.

Common verdigris is prepared in several ways.

1. *French Process.*—The skins and marc of grapes, left after the juice has been pressed out for making wine, are used in France for making verdigris; the material is placed in large tubs, loosely covered over with netting, in which it remains for a few days, when acetic fermentation sets in; when this has commenced sheets of copper (averaging about 8 inches by 4 inches) are thrown in among the fermenting mass—generally old scrap copper is used. They are left in the tub among the grape skins for from 18 to 20 days, the period varying according to the weather;

in summer it may be only about 12 to 14 days, but in winter the longer period named is always required. At the end of the time the tubs are emptied and the grape refuse thrown away; the copper sheets are dried, then dipped into water, or, what is better, into bad wine (if that is obtainable), and again dried; by this means a coat of verdigris is formed on the plates, which is scraped off and placed on one side; the plates are redipped and again dried, when another coating of verdigris is formed, and scraped off as before; the process is repeated until all the copper has been converted into verdigris. The green is washed with water and then dried, when it is ready for use. At one time almost every vineyard in France and Belgium made verdigris somewhat on the above lines, although there were some variations in the minor details; but, as the consumption of verdigris has decreased considerably, its manufacture has not been so generally followed of late years.

2. *English Process.*—In England verdigris is made by packing plates of copper between cloths soaked in the crude pyroligneous acid obtained in the distillation of wood; this is done in casks; every four or five days the casks are unpacked and the cloths redipped in the acid, and the operation repeated until the sheets of copper begin to have a coat of verdigris; they are then dipped in water and dried; the verdigris on them is then scraped off and the copper is again packed with the cloths; and the process repeated until all the copper has been converted into verdigris. The refuse from the manufacture of cider has been used in making this pigment.

The verdigris is finished for use by washing and drying. The latter has to be done very carefully, as too high a temperature would affect the brilliancy of the tint.

Common verdigris is not quite so pure as distilled verdigris; but as it is more insoluble in water and more opaque, it can be used as a pigment.

COMPOSITION AND PROPERTIES OF VERDIGRIS.

—Phillips gives the following analysis of distilled verdigris:—

Copper oxide, Cu O ,	43.25	per cent.
Acetic anhydride, $\text{C}_2\text{H}_3\text{O} \cdot \text{O} \cdot \text{C}_2\text{H}_3\text{O}$,	28.30	„
Water, H_2O ,	28.45	„

which corresponds to the formula



Distilled verdigris is very constant in its composition. It forms dark green crystals somewhat soluble in water and in

acetic acid ; heated in the air they lose their water of crystallisation and their acetic acid, and a black residue of copper oxide, CuO , is left behind. Common verdigris is very variable in its composition and usually contains some impurities ; as a rule, it is generally allowable for commercial verdigris to contain about 2 per cent.

The following analyses of some samples of common verdigris will show the average composition of this pigment :—

	1.	2.	3.	4.	5.
Copper oxide,	44·25	43·79	40·79	43·24	43·5
Acetic anhydride,	29·62	38·49	45·97	27·57	29·3
Water, . . .	23·51	18·00	13·04	29·19	25·2
Impurities, .	2·62	2·0

1 is by Phillips of an English-made sample. 2 and 3 are by the author ; the water in these was present both as hygroscopic and combined water—in No. 2 the amounts were respectively 7·95 and 10·05, in No. 3 they were 4·49 and 8·75. 4 and 5 are by Berzelius of French-made samples.

Verdigris has a greenish-blue colour. It makes but a poor pigment, being the most fugitive of the copper-greens ; in water it soon fades, in oil it is rather more permanent, if kept free from moisture, which causes it to effloresce.

While being almost insoluble in water, it is readily soluble in all acids, without effervescence, to a blue solution, which gives the characteristic tests for copper. Heated with strong sulphuric acid it evolves acetic acid. Heated alone it loses its water and acid and turns black, from the production of oxide of copper.

ASSAY AND ANALYSIS OF VERDIGRIS.—Verdigris may be assayed for tint, covering power, &c., in the usual way.

The following impurities in verdigris should be tested for ; Insoluble matter, carbonates, sulphates, and metals :—

Insoluble Matter, which may consist of barytes, sand, &c., is readily tested for. A weighed quantity is treated with hot dilute hydrochloric acid for a short time and the insoluble matter collected on a filter, dried, and weighed. The amount of insoluble matter should not exceed 3 per cent., and even this is an excessive allowance, as can be inferred from the analyses already quoted ; 2 per cent. is, in the opinion of the author, quite a sufficient allowance, and anything above this ought to be considered as an adulteration.

If, when treating with the acid, effervescence occurs it may be taken as an indication of the presence of *carbonates* either of copper or calcium, or both.

Sulphates can be tested for in the hydrochloric acid solution by adding barium chloride, and their amount may be determined by filtering off, drying, and weighing the precipitate of barium sulphate, which will be formed if they are present.

The presence of *other metals than copper* is best ascertained by working according to the following scheme. The pigment is heated to a red heat to decompose it, and the residue is dissolved in hydrochloric acid and any insoluble matter filtered off; through the solution a current of sulphuretted hydrogen is passed, to precipitate out the copper as the black sulphide; the filtrate is boiled down to a small bulk, a little strong nitric acid is added, and the mixture is boiled for a few minutes; ammonia is then added in slight excess; if any *iron* is present a reddish-brown precipitate will be obtained; this is filtered off and to the filtrate ammonium sulphide is added, which, if *zinc* is present, will throw down a white precipitate of the sulphide of zinc; after filtering this off, ammonium oxalate is added to the filtrate when, if *calcium* is present, a white precipitate of calcium oxalate will be obtained. Calcium may be present either in the form of carbonate or sulphate, which will be inferred from the results of other tests. It is rare for any other metal to be present.

Adulteration of verdigris with Prussian blue can be detected by the blue residue left after the treatment with acid giving all the reactions of Prussian blue. The addition of ultramarine is readily detected by the action of acid on the sample.

Green verditer is sometimes sold under the name of "British verdigris."

SCHEELE'S GREEN.

This pigment was discovered by Scheele, the eminent Swedish chemist, who communicated his method of making it to the Academy of Sciences of Stockholm in 1778. At first it was very much used, being at that time one of the best greens known, but the introduction of emerald-green in 1814 soon brought about its gradual disuse, and now it is doubtful whether it is ever used as a pigment; this is partly due to the fact that it is but a dull colour, while much brighter and better greens are now known; then, again, the fact of its being an arsenical colour has always been much against its use as a pigment.

PREPARATION OF SCHEELE'S GREEN.—1. *Scheele* gave the following instructions for preparing this green:—1 part of powdered white arsenic (arsenious oxide) and 2 parts of potash (carbonate of potassium) are dissolved, by boiling, in 35 parts of

water; the solution is filtered and then poured into a solution of 2 parts of copper sulphate as long as a precipitate falls. The precipitate is collected on a filter, washed with water, and dried at a gentle heat.

2. *Parker* patented, in 1812, a process of making Scheele's green—Two solutions were made in boiling water, one containing 16 ozs. of sulphate of copper, the other 14 drms. of arsenic and 14 ozs. of potash. The precipitate obtained on mixing the solutions was washed and dried. As the alkali is greatly in excess in this process, the precipitate must consist largely of carbonate of copper.

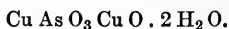
3. *Sharples** prepares Scheele's green by dissolving 2 parts of arsenious oxide (white arsenic) in 8 parts of soda crystals by boiling with 10 parts of water; when dissolved, the arsenite of soda formed is poured into a solution of 6 parts of copper sulphate in 40 parts of water. Both solutions are mixed while boiling, and the mixture itself boiled for a few minutes; it is then allowed to stand until the next day, when the green supernatant liquor is poured off and the green washed two or three times with hot water, dried, and filtered. This is stated to be the most economical process of making the green.

4. *Berzelius* describes a process of preparing a green by boiling copper carbonate with white arsenic; the green has a fine tint.

COMPOSITION AND PROPERTIES OF SCHEEL'S GREEN.—Scheele's green is essentially an arsenite of copper. *Sharples*, who has made a very exhaustive examination of this pigment, states that it is a basic arsenite of copper, usually containing small traces of carbonate and sulphate of copper. He gives the following as the composition of a pure Scheele's green:

Copper oxide, Cu O,	50·00	per cent.
Arsenious oxide, As ₂ O ₃ ,	42 00	„
Water, H ₂ O,	8·00	„

which corresponds to the formula



The pigment as prepared on a commercial scale differs somewhat from this, as might be expected; but the variation is not very great when properly made. The following analyses given by *Sharples* of samples made by Scheele's and *Berzelius*'s processes will show the average composition of this pigment:—

* *Sharples*, *Chemical News*, vol. 35, p. 89 *et seq.*

	Berzelius' Process.	Scheele's Process.	
	1.	2.	3.
Copper oxide, Cu O , .	66·02	50·76	49·25
Arsenious oxide, $\text{As}_2 \text{O}_3$,	8·32	40·82	42·66
Sulphur trioxide, S O_3 ,	...	1·63	0·42
Water, $\text{H}_2 \text{O}$, .	10·33	6·41	6·71
Carbonic acid, C O_2 , .	15·26
	99·93	99·62	99·04

Sample 2 was made according to the original directions; but sample 3 was washed until the wash-waters were free from arsenic.

Scheele's green is of a pale yellowish-green colour, but not very bright; it is quite insoluble in water, but soluble in dilute acids, in dilute solutions of the caustic alkalies, and in ammonia with a blue colour; when boiled with solutions either of the caustic alkalies or of their carbonates it is decomposed, black oxide of copper being deposited; boiling with ammonia does not decompose it. When heated it decomposes, a residue of black oxide of copper being left behind and the arsenic being volatilised.

As a pigment it is not satisfactory; its covering power is small, although it can be used either for oil- or water-colours; it is not permanent and fades on exposure to light and air; in this respect it is rather better than any of the other copper-greens previously described. As a pigment it has gone out of use.

EMERALD-GREEN.

Emerald-green was discovered in 1814, but by whom has not been recorded; from the place at which it was supposed to have been first made it is also known as "Schweinfurth green"; while in America it is largely known as "Paris green," under which name it is mostly consumed as an insecticide on fruit farms. Owing to the brilliancy of its tint, the ease with which it works, and its comparative permanence, it has been extensively used as a pigment. In composition it is an aceto-arsenite of copper, and may be regarded as a compound of verdigris and Scheele's green.

PREPARATION OF EMERALD-GREEN.—1. 125 lbs. of copper sulphate are dissolved in boiling water; 50 lbs. of white arsenic (arsenious oxide) are boiled with a solution of 130 lbs. of

soda crystals until the arsenic is dissolved; this solution while still hot is poured into the copper solution, when a precipitate of copper arsenite will be obtained, and a little carbonate of copper also thrown down; sufficient acetic acid is now added to neutralise all the carbonate and leave a little in excess; the mixture is now allowed to stand for some time for the emerald-green to fully develop; in summer this may take from a week to ten days, in winter it will take about three or four weeks; when formed the green is filtered off, washed, and dried.

2. 8 lbs. of white arsenic is thoroughly mixed with water and then 8 lbs. of verdigris is stirred in; on standing for some time in a warm place emerald-green begins to form; when fully developed it is filtered, washed, and dried.

3. 50 lbs. of copper sulphate are dissolved in water, and to the solution is added 10 lbs. of lime dissolved in 20 gallons of vinegar; to the mixture is added 50 lbs. of white arsenic previously mixed into a paste with water; the mass is allowed to stand in a warm place until the emerald-green has formed, when it is finished as above.

4. *Galloway's Process.*—In the course of an article on emerald-green in the *Journal of Science*, a few years ago, Prof. Galloway described a process for the preparation of emerald-green on rather more scientific lines than either of the above processes, and which gives very good results. This process is carried out in the following manner:—A quantity (100 lbs.) of copper sulphate is dissolved in water, and sufficient sodium carbonate ($28\frac{3}{4}$ lbs. of soda crystals or $12\frac{1}{2}$ lbs. of crystal carbonate) is added to precipitate one-fourth of the copper sulphate used in the form of copper carbonate; then acetic acid is added in sufficient quantity to dissolve this copper carbonate. There is thus obtained a solution containing copper acetate and copper sulphate in about the proportions $3 \text{ Cu SO}_4 + \text{Cu } 2 \text{ C}_2 \text{ H}_3 \text{ O}_2$. The copper sulphate has now to be converted into copper arsenite; to do this the requisite amount of arsenic (60 lbs.) is dissolved by boiling in sodium carbonate (38 lbs. of crystal carbonate or $87\frac{1}{2}$ lbs. of soda crystals), which is rather less than is required to completely precipitate the copper sulphate in the first solution; the two solutions are heated to the boil and then the arsenic solution is run into the copper solution; the green is formed immediately and only requires filtering, washing, and drying, for use as a pigment. The quantities given above have been added by the author, and are not given in the original instructions. When carefully carried out this process gives excellent results.

The fineness of the pigment can be regulated by altering the

strength of the solutions used ; the weaker these are the finer is the precipitate and the more beautiful is the tint of the green produced. If during the precipitation of the green any tendency to form the yellow-green arsenite be noticed, the addition of the arsenic solution is stopped, and the mixture is boiled until all the yellow-green arsenite is converted into the blue-green emerald-green.

5. *M. Camille Koechlin*, in 1886, described in the *Bulletin of the Industrial Society of Mulhouse*, a process for the preparation of emerald-green. 100 grammes of copper sulphate are dissolved in 500 cc. of water ; to this is added 187½ cc. of a solution of arsenite of soda ; this solution contains 500 grammes of the salt in 1 litre of water. A precipitate of arsenite of copper is obtained, and is treated for one hour at from 104° to 122° F. with either 62 cc. of acetic acid of 11° to 12° Tw. or 31 cc. of pure formic acid ; in either case a fine emerald-green is obtained. By using only half the quantity of formic acid a fine blue is obtained, a result which is not got with acetic acid.

6. *Liebig's Process*.—1 part of verdigris is dissolved by heat in acetic acid, then 1 part of arsenious acid, mixed with water, is added, and a yellow-green precipitate is obtained. The mixture is boiled for some time, and the green gradually forms ; if necessary, a little acetic acid should be added from time to time to ensure that all the arsenite is converted into the aceto-arsenite ; too great an excess of acid, however, should be avoided, as it would decrease the yield of emerald-green. As soon as the green is fully developed it is filtered off, washed, and dried.

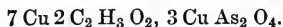
The drying of emerald-green must be done at as low a temperature as possible, as heat causes the tint to deteriorate.

Emerald-green is by no means a difficult colour to make ; the first process described takes some time, but the last three are quick processes and give good results.

COMPOSITION AND PROPERTIES OF EMERALD-GREEN.—Emerald-green is an aceto-arsenite of copper of somewhat variable composition, according to the process by which it has been made. The following analysis of a sample of English-made emerald-green will serve to show the average composition of this pigment :—

Copper oxide, Cu O ,	32·55 per cent.
Arsenious oxide, $\text{As}_2 \text{O}_3$,	57·51 „
Acetic anhydride, $\text{O} 2 \text{C}_2 \text{H}_3 \text{O}_2$,	6·63 „
Sulphur trioxide, S O_3 ,	1·67 „
Water, $\text{H}_2 \text{O}$,	0·90 „

Leaving out of consideration the impurities, the formula for emerald-green deducible from the above analysis is—



Emerald-green is a bluish-green of a very fine tint, quite different from any other known pigment, and very difficult to imitate; it is very opaque, and hence has good covering power; it works well in both oil and water, but best in the latter; kept in a dry place it is fairly permanent, and resists exposure to light and air, but in a damp place it turns brownish.

It is soluble in acids to blue solutions; in ammonia it also dissolves with the characteristic copper-ammonia colour; in solutions of caustic soda and potash it is also soluble; on boiling, a red precipitate of cupreous oxide falls down, a characteristic reaction of emerald-green.

Emerald-green cannot be mixed with pigments—such as cadmium-yellow, ultramarine, &c.—which contain sulphur, as this causes its discolouration, owing to the formation of black copper sulphide. With other pigments it can be mixed without any alteration. The use of emerald-green has been on the decrease of late years, partly owing to its poisonous character, due to its containing arsenic, although one authority states that there is no foundation for the statement that emerald-green is poisonous, and says that it has no poisonous properties whatever. The accounts of the poisonous action of emerald-green are very conflicting; some persons are much affected by emerald-green; even going into a room covered with paper printed with this pigment is sufficient to produce poisonous symptoms in them, while others are not affected at all; arsenic seems to be very peculiar in its toxic action, and much depends upon the physiological idiosyncrasies of the person.

ASSAY AND ANALYSIS OF EMERALD-GREEN.—The colour or tint, body, and colouring power of emerald-green should be assayed for in the usual way.

To test for the purity or otherwise of a sample of emerald-green the following tests can be applied:—In hydrochloric acid it should completely dissolve with a yellow-green colour, and on diluting with water this colour should turn bluish. It dissolves in ammonia with a deep blue colour. In caustic soda it dissolves to a pale blue solution, from which, on boiling, a red precipitate of cupreous oxide falls down. The solution in hydrochloric acid should not give more than a faint precipitate with barium chloride, showing the absence of sulphates; through the solution a current of sulphuretted hydrogen should be passed for some

time and the precipitate of copper and arsenic sulphides obtained filtered off; the filtrate after boiling, to free it from excess of sulphuretted hydrogen, should give no further precipitate on the successive addition of ammonia, ammonium sulphate, and ammonium oxalate, showing the absence of metals, such as iron, zinc, and calcium.

The presence of arsenic in emerald-green or other pigments is best detected by Marsh's test. This is carried out as follows:— Provide a wide-mouthed bottle and fit it with a tight-fitting cork through which a piece of glass tube drawn out to a point is passed. Into the bottle, water, zinc, and sulphuric acid are placed. It is necessary that the two latter bodies be free from arsenic, as the ordinary commercial articles are very liable to contain arsenic which would interfere with the proper testing of any pigment for arsenic. By the action of the acid on the zinc hydrogen is evolved; this may be lighted as it issues from the glass jet, and will burn with a non-luminous flame. On pressing a piece of white porcelain down on the flame no brownish-black spot should be produced. The gas must not be lighted immediately it begins to issue from the jet, but a few minutes should be allowed to elapse before doing so, to allow the air in the bottle to be completely driven out; otherwise an explosion may ensue. If, after it has been proved that the gas flame produces no spot on a porcelain plate, the sample to be tested for arsenic be introduced into the bottle and the gas re-lighted, it will now be found to burn with a faintly luminous flame and will give a blackish-brown metallic looking spot on a piece of white porcelain pressed down on the flame; this stain is soluble in a solution of bleaching powder. Very small traces of arsenic can be detected by this test. Another test for arsenic is Reinsch's, which consists in heating the sample with hydrochloric acid and a clean copper plate; if arsenic is present the latter becomes covered with a grey deposit.

MINERAL GREEN.

Under this name and that of Mountain green is offered for use as a pigment the natural green mineral known as Malachite. There is also an artificial green pigment made under the name of mineral green.

Mineral green, Mountain green, Malachite is a natural basic carbonate of copper found in many places—Cornwall, Siberia, Persia, Australia, &c. The ordinary commercial product comes from Siberia where it is found in the greatest abundance and in

large masses of a very fine colour. For use as a pigment the natural mineral is simply ground as finely as possible.

The mineral exists in two forms—in the one it forms compact masses of a fine yellowish-green tint; in the other form it is rather paler and more porous or powdery in character; the former is the most valuable as a pigment.

In composition it is a basic carbonate, containing on the average

Copper oxide, Cu O ,	. . .	71.9	per cent.
Carbonic acid, C O_2 ,	. . .	20.0	„
Water, $\text{H}_2 \text{O}$,	. . .	8.1	„
		100.0	

and having the formula $\text{Cu C O}_3 \cdot \text{Cu H}_2 \text{O}_2$.

It makes a good pigment, is fairly permanent, and works well both in oil and water. Its faults are those common to all copper pigments.

It dissolves in acids with effervescence and evolution of carbonic acid, and the solution gives all the characteristic tests for copper.

Mineral green has been made artificially by several processes, of which the following are two examples:—

(a) For preparing mineral green by this method the following materials are required:—2 cwts. of soda crystals, $1\frac{1}{2}$ cwts. of blue stone (copper sulphate), 70 lbs. of quicklime, $12\frac{1}{2}$ lbs. of white arsenic, and 4 ozs. of tartaric acid. Boil the arsenic and soda together until the former is dissolved; dissolve the copper in water; and slake the lime in water. Add the lime to the copper solution; then the arsenic and soda; and, finally, the tartaric acid. Keep the whole at a temperature of about 150° to 160° F. for some time until the colour is properly developed, then wash the pigment with clean water, filter and dry at a low temperature.

(b) 14 ozs. of potash and 14 drms. of arsenic are dissolved in water; 1 lb. of sulphate of copper is dissolved separately in 2 gallons of water, and into this solution is poured the arsenic and potash solution; the green is precipitated and is collected and finished in the usual way.

No process of making mineral green artificially produces it of the same deep green tint as the natural variety; such prepared greens have a pale yellowish-green tint and are not so permanent as the natural variety. In their general features they resemble the verditer greens, but are rather brighter in tint and deeper in colour.

GREEN VERDITER.—This pigment is a basic carbonate

of copper, prepared by precipitating solutions of copper with the carbonates of potash or soda in the same way as blue verditer is made. It has a pale tint of a somewhat yellow tone of green. As a pigment it has no great use, and has become nearly obsolete; it is not permanent, either as an oil or a water colour.

Green verditer has also been known as "British verdigris," and its preparation under this name has been patented.

BREMEN GREEN.—This is of a pale green tint, prepared in the same way as Bremen blue, except that the final blueing is omitted. Like green verditer it is essentially a basic carbonate of copper. Its use as a pigment has become obsolete.

PROPERTIES OF THE COPPER GREENS.—With one or two exceptions, the copper greens are by no means satisfactory pigments; their colour is but pale and not brilliant, except emerald-green and the natural mineral green. Their covering power is also deficient; they mix with either oil or water. They are not permanent, as exposure to light and air causes them to fade, while sulphuretted hydrogen and sulphur compounds cause them to go black, owing to the formation of the black sulphide of copper; hence they cannot be mixed with any pigments containing sulphur—such as cadmium yellow, King's yellow, ultramarine, &c. Strongly alkaline bodies, such as lime, change their colour to a blue.

Heat decomposes all the copper greens, the acid portion—carbonic, acetic or arsenious—being volatilised, and a black residue of oxide of copper being left behind.

They are all soluble in acids, some with effervescence, indicating the presence of a carbonate; the solutions have a blue colour, to which ammonia imparts a characteristic deep blue tint; on adding caustic soda a blue precipitate is obtained, which, on boiling, turns black. Sulphuretted hydrogen gas passed through the solutions throws down a black precipitate of the sulphide, which is soluble in nitric acid to a blue solution.

TERRE VERTE.

Terre verte is the name given to green pigments of an earthy character, found naturally in various places; in some cases, the pigment has been named after the place where it was found, as "Verona green," "Verona earth," &c. These natural greens are usually of a pale greyish-green tint, and are only useful on account of their permanence. Deposits of green earth are found in many places, but only the deep bright samples are usable as pigments. The places where the best qualities of terre verte are found are

the Mendip Hills, as also many localities in France, Italy, and Cyprus.

Terre verte is found in masses of a more or less compact character; some varieties are soft and easily powdered, others are harder and more vitreous in appearance. For use as a pigment, the mineral is ground up as fine as possible; sometimes it is levigated.

Although varying somewhat, as might be expected in earthy pigments from various sources, yet there is a certain amount of resemblance between different samples of terre verte, as shown by the few analyses of this pigment available. Berthier gives the following analysis of terre verte, the source of which is not stated:—

Silica, Si O_2 ,	51·21 per cent.
Ferrous oxide, Fe O ,	20·72 ,,
Soda, Na_2O ,	6·21 ,,
Alumina, Al_2O_3 ,	7·25 ,,
Magnesia, Mg O ,	6·16 ,,
Water, H_2O ,	4·49 ,,
Manganese, Mn O_2 ,	trace.
	<hr/>
	96·04

This is not a very satisfactory analysis; of what does the 4 per cent. of unaccounted for material consist?

A sample of terre verte from Cyprus, analysed by Klaproth, gave the following figures:—

Silica, Si O_2 ,	51·5 per cent.
Ferrous oxide, Fe O ,	20·5 ,,
Potash, K_2O ,	18·0 ,,
Magnesia, Mg O ,	1·5 ,,
Water, H_2O ,	8·0 ,,
	<hr/>
	99·5

A sample of terre verte from the neighbourhood of Rome was examined by the author, and found to have the following composition:—

Water, hygroscopic, H_2O ,	1·450 per cent.
Water, combined, H_2O ,	3·650 ,,
Ferrous oxide, Fe O ,	26·870 ,,
Alumina, Al_2O_3 ,	3·165 ,,
Manganese, Mn O_2 ,	trace.
Calcium oxide, Ca O ,	2·065 ,,
Silica, Si O_2 ,	52·120 ,,
Magnesium oxide, Mg O ,	10·665 ,,
	<hr/>
	99·985

This sample was very hard, and had a conchoidal fracture, a waxy lustre, and a soapy feel. Acids had but slight action on it. It was evidently a specimen of the mineral bronzite, which is essentially a ferrous magnesium silicate.

Terre verte is of a pale bluish-grey tint, and has no great colouring power or body, being somewhat transparent; it mixes well with either oil or water, and is perfectly permanent, being unaffected by any length of exposure to light and air; it is not altered by sulphur or sulphureous gases in any way. As a pigment terre verte has been used from very early times, being one of the best greens available to the early painters. Heat turns the colour of terre verte to a reddish-brown, the change being similar in nature to that which takes place when the ochres are heated.

Sometimes greens having a copper base are offered as terre vertes; these are not permanent.

COBALT GREEN.

Cobalt green, Rinman's green, Zinc green is a compound of the oxides of zinc and cobalt, having an analogous composition to cobalt blue and being prepared in a similar manner.

Preparation of Cobalt Green.—Cobalt green can be prepared in several ways.

(a) Sulphate of cobalt in solution is mixed with zinc oxide into a paste; this is then dried and exposed to a red heat in a muffle furnace until the desired green tint has been developed, which will take from three to four hours. The tint of colour will depend upon the proportions of the cobalt salt and zinc oxide used; 1 lb. of cobalt sulphate to 5 lbs. of zinc oxide will give a deep green; with twice as much zinc oxide a grass green is obtained; while if the proportions are 1 lb. of cobalt sulphate to 20 lbs. of zinc oxide a fine bluish-green is obtained, which forms a fair substitute for emerald-green.

(b) Instead of the sulphate, the nitrate of cobalt may be used. 1 lb. of cobalt nitrate is mixed with 2 to 5 lbs. of zinc oxide according to the depth of colour required; the mixture is kept at a bright red heat in a muffle furnace for a few hours until the green has been fully developed; it is then ground with water, and dried. The cobalt salt must be free from metallic impurities, such as iron, alumina, or tin.

The principal difficulty in these two processes is that of ensuring a thorough mixture of the cobalt and zinc compounds; if this is not properly done the green which is formed will not be

of a uniform tint throughout the mass ; there will be dark and light places. The following processes avoid this difficulty by mixing solutions of the two metallic salts, thereby ensuring perfect admixture, then precipitating the oxides from the solution and finishing as in the above processes :—

(c) 1 lb. of nitrate of cobalt or $\frac{1}{2}$ lb. of the chloride of cobalt and 6 lbs. of sulphate of zinc are dissolved in 7 gallons of water ; a solution of carbonate of soda is then added as long as a precipitate falls ; the mixture filtered, and the precipitate of hydroxides of cobalt and zinc so obtained washed, dried, and heated as before. By varying the proportions between the zinc and cobalt salts the depth of colour of the resulting green can be varied to a great extent.

(d) Instead of using the carbonate of soda to precipitate the solution of zinc and cobalt, there may be used either the phosphate or the arseniate of soda. Wagner states that the resulting green is purer, brighter, and less dense. The greens made in this way will contain phosphoric acid, which will give the greens a rather bluer tint.

Cobalt green has a bright green colour of a slightly yellow hue. It is perfectly permanent when exposed to light and air, and is on that account a useful pigment. It can be mixed with all other pigments without being affected by them or altering them in any way. It is unacted upon by acids in the dilute state ; but strong acids decompose it, forming a blue solution. Alkalies have no action on it.

Wagner gives the following analyses of cobalt green made by various processes :—

	1.	2.	3.
	Per cent.	Per cent.	Per cent.
Zinc oxide, Zn O, . . .	88·040	71·93	71·68
Cobalt oxide, Co O, . . .	11·622	19·15	18·93
Phosphoric oxide, P ₂ O ₅ ,	8·22	8·29
Ferric oxide, Fe ₂ O ₃ , . . .	0·298
Soda, Na ₂ O,	0·69	...
	<hr/>	<hr/>	<hr/>
	100·000	99·99	98·90

Owing to its cost cobalt green is not much used. Should it be possible to find a cheap source of cobalt this green might come into more general use, as its permanent qualities would give it superiority over many of the other greens.

Besides the greens described above many others have been used on a small scale ; some are still used for special purposes, and others have been described by various chemists, but whether they

have ever been used on a practical scale is doubtful; these will be briefly described.

BRIGHTON GREEN is the name given to a pigment made by grinding together in the dry condition 7 lbs. of copper sulphate, 3 lbs. of acetate of lead, and 24 lbs. of whiting; during the grinding chemical decomposition sets in, resulting in the formation of a basic acetate of lead. It was a pigment of no great depth of colour or permanency.

DOUGLAS GREEN.—Mr. Thomas Douglas has described in the *Chemical News*, vol. xl., p. 59, a green prepared from barium chromate. The latter compound, prepared in the usual way by mixing solutions of barium chloride and potassium chromate, is mixed with 20 per cent. of its weight of strong sulphuric acid, which partially decomposes it, forming a mixture of barium chromate, chromic acid, and barium sulphate; the mixture is dried and then calcined at a bright red heat in a crucible; the chromic acid is thereby decomposed into the green oxide of chromium, which, being disseminated throughout the mass of barium sulphate and chromate, colours it green, forming a pigment possessing considerable body and permanency. Nothing definite is known as to its having been used as a pigment.

CHINESE GREEN or LOKAO.—This is a green pigment, as yet but little used, made from the juice of various Chinese species of buckthorn trees by extracting the juice from the berries by pressure, mixing this with alum, &c., and drying. It comes into commerce in the form of bluish-green slabs, which are easy to break, but somewhat difficult to powder. Chinese green contains from 27 to 47 per cent. of mineral matter, principally lime and alumina, and, probably, consists of the lake formed by the combination of those bases with the colouring principle of the juice from the buckthorn berries, named by Kayser lokaonic acid, $C_{42}H_{48}O_{27}$. According to the same authority, the colouring principle consists of a glucose, which he calls lokaose, to which he assigns the formula $C_6H_{12}O_6$, and lokaonic acid, a body having the composition $C_{33}H_{36}O_{21}$. The colouring principle has also received the name lokain and the formula $C_{28}H_{34}O_{17}$.

SAP GREEN.—This pigment is prepared from buckthorn berries. Two methods are adopted in its preparation. In one the berries are allowed to ferment slightly by placing them in a warm place for a few days; they are then pressed, the juice collected, and alum added in the proportion of from $\frac{1}{2}$ an ounce to 1 ounce per pound; the mixture is then boiled down and evaporated to dryness at the boiling heat. Another plan is to

boil the berries in water for two or three hours with constant stirring; the liquors are then strained through cloths in order to separate the woody and other insoluble particles; the clear liquor is boiled down to a syrup, 5 ozs. of alum per gallon added to the syrup, and the mixture carefully evaporated to dryness. For some purposes the mass is left in the pulpy condition.

Sap green is a dark yellowish-green pigment; when dry it breaks with a glossy fracture; it is very transparent, and hence is not used as a body colour, but chiefly as a glazing colour; another use for it is in colouring confectionery and beverages.

It works well as a water-colour, but not as an oil-colour; and fades on exposure to light.

An analysis of sap green made by the author shows it to have the following composition:—

Water,	12·95 per cent.
Mineral constituents,	10·69 „
Organic constituents,	76·36 „
	<hr/>
	100·00

Of the organic constituents a quantity equal to about 29·34 per cent. of the original colour are soluble in alcohol. Its composition and general properties somewhat resemble those of a lake.

MANGANESE GREEN.—This pigment was patented in 1864 by *Schad*, who prepared it by the following process:—14 parts of oxide of manganese, 80 parts of nitrate of barium, and 6 parts of sulphate of barium, are intimately mixed together. The mixture is heated in a crucible in a suitable furnace to a bright red heat until it has assumed a green colour; it is then ground in a mill with water to a fine powder; a small quantity of gum arabic, dextrine, or similar substance, amounting to about 5 per cent. of the original material, is added, and the mass is dried at from 190° to 212° F.; or it may be used in the form of a paste. Instead of the above mixture there may be used one of 24 parts of nitrate of manganese, 46 parts of nitrate of barium, and 30 parts of sulphate of barium. The addition of the gum or dextrine is said to be essential for its stability, a factor which cannot but have an adverse influence on its value as a pigment, for which purpose it has probably not been used. It consists principally of manganate of barium.

TITANIUM GREEN.—This pigment is the ferrocyanide of titanium, prepared by mixing solutions of potassium ferrocyanide and of a titanium salt; the pigment must be dried at a low temperature, as decomposition sets in above 100° C. It has a pale

green colour, and was proposed as a substitute for the arsenical greens; owing to its cost it has never come into use.

ZINC GREEN.—Under this name there is frequently sold greens made in a similar way to the Brunswick greens, by mixing together zinc chrome, Prussian blue, and barytes; such greens possess the advantage that they are not affected by sulphur as much as the Brunswick greens. They are best made in the dry way (see p. 151).

The green lakes and the pigments made from coal-tar colouring-matters will be found described in the chapter on Lakes.

CHAPTER VI.

BLUE PIGMENTS.

Blue, as a colour, enters very largely into the decoration of objects, both alone and in combination with other colours, to form a large and very useful series of tints and shades. Although so important as a colour, yet there are few blue pigments; but these possess the merit of being more permanent, and, therefore, more useful than any other group of pigments. The list of blue pigments includes ultramarine (a curious compound of silica, alumina, and soda, which was at one time obtained exclusively from natural sources, but is now mostly prepared artificially), and Prussian blue with its varieties (a most valuable blue, whose base is iron), which are the most predominant blue pigments used. Cobalt is the base of cobalt blue and smalts, while copper forms the basis of several unimportant pigments.

ULTRAMARINE.

Ultramarine is one of the most important pigments possessed by the painter; being used in painting, in printing of all kinds (letterpress, wall-papers, calico), and in bleaching; it is undoubtedly the best blue for the laundry, and in soapmaking it is used to produce the blue mottled soap.

Ultramarine has been known for centuries, but its extended use has only been possible during the last half century. Prior to about 1820 the natural supplies were small, and the processes so expensive that it could only be used by artists who did not find the cost prohibitive; but about the year named, discoveries were made by several chemists, which resulted in ultramarine being made artificially at such a cheap rate that it is the cheapest blue pigment known; consequently, its consumption is now measured by tons.

Natural Ultramarine.—The source of natural ultramarine is a blue mineral, lapis lazuli, found in small quantities in Persia, China, Siberia, and a few other places. This mineral is found in streaks and small patches distributed through an earthy matrix

or gangue, from which it has to be separated by mechanical means. The production of natural ultramarine has declined very much during the last fifty years, it having been displaced by artificial ultramarine; but the mineral is still sought for in fair quantities, for use in the production of inlaid ornamental work, as the peculiar blue colour of the mineral cannot be obtained by other means.

The process of extraction of the pigment from the mineral consists in grinding the mineral to a fine powder, after separating as much of the gangue as possible; it is then mixed with a compound of resin, wax, and linseed oil, and the mixture put into cloths and kneaded under hot water; the colour comes through the cloth into the water, several waters being used; after the working, the waters are placed on one side for the colour to settle. The blue thus obtained varies in shade in the different waters; that which settles out of the first water is the deepest in colour, and the brightest, and is sold as ultramarine; that which comes from the last waters has a blue-grey colour, and is sold as ultramarine ash. After the colour has settled, it is usual to grind it still finer, so that the beauty of the pigment shall be developed as much as possible. No better process for extracting ultramarine has been devised, although it is so tedious and gives such poor results. Very little is now so produced, as the natural variety has been almost replaced in European and other countries by the artificial variety.

The chemical composition and constitution of ultramarine early became the subject of research by chemists, which researches were partly undertaken with a view to its artificial production; for it was recognised that, from the beauty of its colour and its permanent qualities, ultramarine would, if it could be produced cheap enough, have a wide field of use. Several analyses were made by different chemists, but these vary very much, owing, as is probable, to the difficulty of obtaining the pigment quite free from its matrix. Those by Clement and Desormes and by Gmelin, which are, perhaps, the most typical, are here given.

	Clement and Desormes.	Gmelin.
Silica, Si O_2 ,	35·8	47·306
Alumina, $\text{Al}_2 \text{O}_3$,	34·8	22·000
Soda, $\text{Na}_2 \text{O}$,	23·2	12·063
Sulphur, S,	3·1	0·188
Calcium carbonate, Ca C O_3 ,	3·1	...
Calcium oxide, Ca O ,	1·546
Sulphuric acid, $\text{H}_2 \text{S O}_4$,	4·679
Water and loss,	12·218
	<hr/>	<hr/>
	100·0	100·000

It is evident that with such discrepancies in the analyses nothing could be satisfactorily inferred as to the chemical composition and constitution of ultramarine, and it is no wonder that none of them led to its artificial production.

Artificial Ultramarine.—Early in the present century, soon after soda began to be produced on the large scale from salt by the Leblanc process, many persons noticed the formation of a substance resembling ultramarine in colour; Tessart and Kuhlmann recorded, in 1814, that they had seen this blue colour in a soda furnace. Vauquelin, on examining it, found it to be a compound of silica, alumina, lime, soda, and sulphur, and showed that it had a similar composition to ultramarine. It was recorded that it was formed only when sandstone was used in the construction of the furnace; when bricks were used it was not formed.

Guimet, an eminent French manufacturing chemist, studied the production of ultramarine. In 1828 he succeeded in making it on a large scale, and obtained a prize of 6,000 francs, offered by the Société d'Encouragement of France to any one who made ultramarine in a wholesale way. Guimet's process is still used by his successors, but has not been published.

Gmelin also interested himself in the production of ultramarine, and in 1828 he published an elaborate description of his method of making it.

Kottig, the director of the Miessen Porcelain Works also, about the same time, observed the production of ultramarine in his furnaces, and, as the result of his researches, succeeded in making the pigment on a large scale; the Miessen ultramarine was for many years one of the leading brands; the works are now closed.

About 1834 Dr. Leverkus, working by Gmelin's process, started its manufacture in Germany at works which are still in existence.

The great bulk of the ultramarine used is made in Germany; there are two or three works in England, a few in France, and one in America. Several writers have given descriptions, more or less complete, of the process of making ultramarine; but the best and most complete description is that by J. G. Gentele,* and more recently one by Rawlins.†

Varieties of Ultramarine.—There are two principal varieties of artificial ultramarine—1st, sulphate ultramarine, which is of

* *Technologiste*, vol. xviii., pp. 389-411.

† *Journ. Soc. Chem. Ind.*, 1887, p. 791.

a pale greenish-blue colour; 2nd, soda ultramarine, which has a violet-blue colour. Of the latter there are two varieties—one contains more silica than the other, and is mostly used by paper-makers, owing to its resisting the action of acids and alum better, while the variety poor in silica is used for all other purposes.

The materials used are nearly the same for both kinds, and comprise kaolin or china clay, sodium sulphate (Na_2SO_4), sodium carbonate (Na_2CO_3), sulphur, coal or charcoal, rosin, quartz, and infusorial earth. All these are not used in the same operation; some makers using one kind of mixture, others another. The quality of the materials is a matter of very great importance.

The kaolin or china clay should be as free as possible from any earthy matrix; a trace of lime has no injurious influence, but the clay must be free from iron, which has a tendency to dull the colour of the ultramarine. It has been found from experience that every sample of china clay does not give equally good results, although all may be pure and of good quality. It has been found that the relative proportions in which the silica, SiO_2 , are combined with the alumina, Al_2O_3 , is a matter of some importance, and in china clays from different localities there is wide differences in this respect; then, again, a china clay which will work well for sulphate ultramarine will not do for soda ultramarine. For making sulphate ultramarine the china clay should contain the silica and alumina in the proportion of 2 silica to 1 alumina, 2SiO_2 , Al_2O_3 ; if the proportions much exceed these the shade will be poor, while if they reach those indicated by the formula, 3SiO_2 , Al_2O_3 , the clay will not make sulphate ultramarine. On the other hand, while almost all clays will make soda ultramarine, yet the best results are obtained with clays containing from $2\frac{1}{2}$ to 3 parts of silica to 1 part of alumina; the larger the proportion of silica, the redder the shade of the ultramarine made from it, and the more resisting power it has to the action of acids and alum. The china clay is prepared for use by a process of grinding and levigating, so as to obtain it in as fine a form and as free from impurity as possible.

The sodium salts are used in the anhydrous state; both should be as pure as possible, especially should they be free from iron, which has a most deleterious influence upon the shade of the ultramarine made from the salts. Although other impurities are of small moment, still, where first-class ultramarine is required, it is best to purify the commercial products.

The sulphur is the ordinary roll sulphur or brimstone.

The coal and charcoal are the ordinary commercial varieties ; but the coal used must be free from pyrites. Both articles are ground before using.

The quartz should be as free from impurities as possible ; the better the quality of the quartz, the better the quality of the ultramarine made from it.

The infusorial earth or kieselguhr is the well-known commercial article.

The rosin used is the best commercial variety obtainable.

The manner in which these are mixed together depends upon the variety of ultramarine to be made, and it also varies in different works, each of which has its own formula, although there is not much variation in the essential points.

Gentele lays down the following rules:—1st, That the soda used be sufficient to neutralise half the silica present in the kaolin or clay and silica used ; 2nd, that the proportions of soda and sulphur be such as to produce a polysulphide of soda.

ULTRAMARINE MANUFACTURE.—There are two processes in use for the manufacture of ultramarine ; the oldest, called the indirect process, is used for making both sulphide and soda ultramarines, and is the only process by which the former can be made.

Indirect Process of Making Ultramarine.—This consists of the two stages or operations, viz. :—

- (a) The calcining operation.
- (b) The colouring operation.

(a) **Calcining Operation—Manufacture of Ultramarine Green.**—A mixture of the ingredients named above is made ; if sulphate ultramarine is required, sulphate of soda is used ; if soda ultramarine is to be made, then soda carbonate is used. Some works use a mixture of the two soda salts.

The various ingredients are ground together with water into a very fine paste ; the finer the grinding, the better will be the quality of the ultramarine ; after the grinding, the paste is dried. In some works the water is omitted, it being considered unnecessary, while the subsequent drying adds to the expense of making.

The following are examples of the mixings used in different works :—

For sulphate ultramarine.

	1.	2.	3.
	Parts.	Parts.	Parts.
Kaolin,	100	100	100
Sodium sulphate,	83	41	220
Coal,	17	17	...
Sodium carbonate,	41	...
Sulphur,	13	30
Rosin,	35

When sodium sulphate is used less sulphur is required ; in proportion as the latter is decreased so the proportion of the former must be increased.

For soda ultramarine poor in silica—

Kaolin,	100 parts.
Sodium carbonate,	100 ,,
Coal,	12 ,,
Sulphur,	60 ,,

For soda ultramarine rich in silica—

	1.	2.
	Parts.	Parts.
Kaolin,	90	100
Quartz,	10	...
Sodium carbonate,	100	90
Sulphur,	60	100
Coal,	12	4
Rosin,	6

The second recipe gives a dark ultramarine ; the more sulphur there is used in making soda ultramarines, the deeper is the shade of the blue produced ; on the other hand, by reducing the quantity of sulphur and silica the blue obtained is not so deep, but is rather more brilliant in hue.

The mixture is then placed in crucibles, about 6 inches by 4 inches in size, and fitted with lids, which are somewhat saucer-shaped, so that the crucibles can be piled one above another in a furnace. Fig. 19 shows the shape of the crucible and its lid.

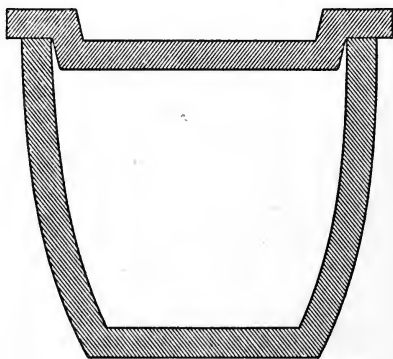


Fig. 19.

The mixture is packed rather tightly into these ; sometimes what are called seggars are used, but the crucible form is better, as giving

a firmer pile when placed in the furnace. In some works open, flat, round capsules are used of such a size that they hold when $\frac{3}{4}$ full, about 9 ozs. of the material, which forms a layer $1\frac{1}{4}$ to $1\frac{3}{4}$ inches thick; these are piled one above the other in a furnace capable of holding about 216 arranged in 9 layers of 24 capsules, each formed of lots of 6 by 4.

The furnace in which these pots of material are placed varies in form in different works. Fig. 20 shows one form of ultramarine furnace. The furnace chamber, B, is an almost exact

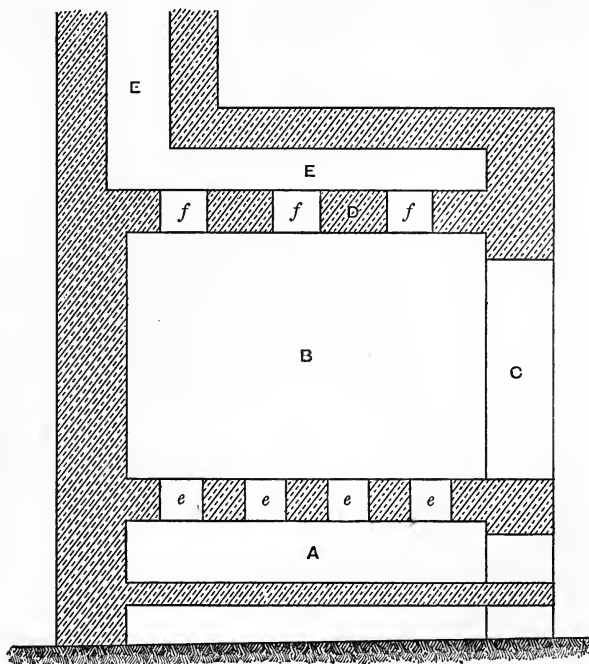


Fig. 20.—Ultramarine furnace.

cube in form; the back is completely closed in, and the front, C, is open, but is made up with firebricks when the furnace has been filled with the crucibles. The fireplace, A, is under the furnace chamber, the flames and heat in it pass through openings, *e e e*, in the floor of the chamber; similar openings, *f f*, in the roof, D, of the chamber serve as outlets for the waste heat and gases

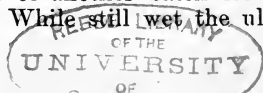
of the furnace into the flue, E E. A number of these furnaces are built side by side and back to back, forming a range or bench of furnaces, but are not all worked together, for while some are being filled, others are being emptied, and others, again, are being heated. In some works a kind of muffle furnace, similar to Fig. 21, is used.

After the furnace has been charged with the crucibles, the front is made up with bricks, and the interstices between these filled with a mixture of sand and clay, a small sight-hole being left so that the temperature of the furnace can be observed; if necessary, this sight-hole is stopped with an easily removable plug of clay. The temperature of the furnace is then slowly raised to a bright red heat, at which it is maintained for from 7 to 10 hours, the time varying with the nature of the composition and determinable only by actual practice. Sulphate ultramarine requires a higher temperature than soda ultramarine; if a muffle furnace is used, the temperature is often raised to a bright yellow for from $2\frac{1}{2}$ to 3 hours only.

When the calcination is considered to be complete the fire is drawn and the furnace allowed to cool; this must be done as slowly as possible, and care must be taken that no air enters into the furnace during the cooling, because while hot the crude ultramarine is very susceptible to the action of the oxygen of the air, and the yield as well as shade of the colour would be injured. When cold the crucibles are removed and the furnace is ready for another charge. This first burning of the ultramarine is a most important operation, and great care must be exercised in carrying it out; access of air to the contents of the crucible must be carefully avoided; the temperature should not be too high nor too prolonged, as then the material would be overburnt and will not give a satisfactory blue; on the other hand, underburning is just as bad, for then the colour will not be homogeneous. A furnace such as that shown can be charged three times per week.

The colour of the burnt mass varies somewhat; usually it is of a green colour, mostly of a bluish tone (which is generally indicative of good burning), but sometimes it is of a yellowish-green shade, and at others it passes more into a blue, while, if not properly burnt, it will have a brown shade.

The crude green ultramarine, which is somewhat cindery in appearance, is now thrown into water for the purpose of washing out all the soluble soda salts; the last washings of one batch are often used as the first wash-waters of another batch for the purpose of economising the water. While still wet the ultra-



marine is ground up in mills into as fine a form as possible, in order to effect the completest practicable extraction of the soluble matter. The ground-up green ultramarine is then dried, when it is ready for the next operation. In this form it is sold under the name of green ultramarine for use as a pigment.

The wash-waters contain a large proportion of sodium salts, chiefly in the form of sodium sulphide. In many works it is customary to evaporate the liquors to dryness by means of the waste heat of the furnaces, and to use the dry residue for another mixing.

(b) Colouring Operation—Manufacture of Ultramarine Blue.—The green ultramarine obtained in the first stage has now to be converted into the blue, which is done by heating it with sulphur in a furnace at a low temperature.

There are three ways of carrying out this colouring operation.

(1) On trays, (2) in a cylinder, and (3) in a muffle.

1. *Tray Method.*—A form of muffle furnace is built in which the muffle is filled with a number of trays or shelves. On these trays the green ultramarine is spread in layers of about an inch thick, and over them is sprinkled some sulphur; the muffle door is closed, the furnace is lighted, and the heat continued until the sulphur takes fire; then the fires are drawn and the sulphur allowed to burn itself out, after which the crude pigment is taken from the muffle and finished in the manner described further on.

2. *Cylinder Method.*—It is also known as the German method. Small cast-iron cylindrical vessels are imbedded in brickwork over an ordinary fireplace; these cylinders are closed at the back end, but open in front, which is fitted with a door made of wrought iron; in this door are two apertures for the purpose of charging the cylinder with sulphur, while a pipe from the top of the cylinder carries off the gases produced by the burning of the sulphur. An agitator is fitted to the cylinder, by means of which its contents can be kept well mixed during the progress of the operation.

From 27 to 34 lbs. of the ground green ultramarine is charged into the furnace, the door closed and the fire lighted. When the temperature is sufficient to ignite sulphur, 1 lb. of sulphur is thrown into the cylinder; when this has burned away and fumes have ceased to issue from the cylinder, another pound of sulphur is thrown in and allowed to burn; a small sample is now drawn from the furnace and its colour noted; if not blue enough, more sulphur is thrown in at intervals until a sample taken out of the cylinder shows that the blue has properly formed; after the cylinder has cooled down the pigment is scraped into a box, and is ready for the finishing operation.

During the whole of this operation the temperature of the furnace is kept at the proper heat, viz., that at which sulphur will burn, and the agitator is kept at work.

3. *Muffle Method.*—It is also known as the French method. In this method the green ultramarine is coloured by heating with sulphur in a muffle furnace. Such a furnace is shown in Fig. 21, which represents a longitudinal section of an ultramarine muffle furnace. The fireplace is shown at A, and is separated from the

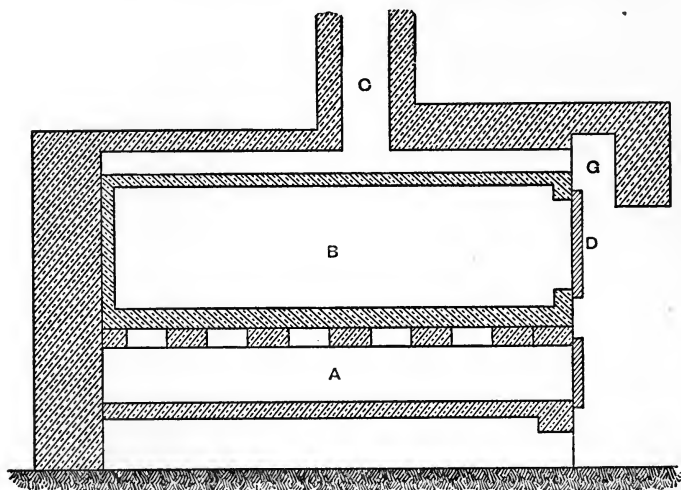


Fig. 21.—Ultramarine muffle furnace.

muffle-chamber by a flued arch. The muffle, B, is made of earthenware, and is completely closed at one end, while the other is fitted with a door, D, so built into the furnace that none of the furnace gases can get into the interior of the muffle; C is the flue of the furnace; G is a kind of hood which collects all the vapours of the burning sulphur, and passes them into the flue, C, and so up the general chimney of the works.

The green ultramarine is spread in a layer of about $1\frac{1}{2}$ to 2 inches thick on the floor of the muffle, the door closed and the fire lighted; when the temperature is high enough for sulphur to burn, a shovelful of that substance is thrown into the muffle and stirred with an iron rod; when the first shovelful has burnt out, more sulphur is added from time to time, until a sample of the colour taken out of the furnace shows that it has acquired the

desired blue colour. The muffle is more rapid in working than the cylinder. The blue is raked out of the furnace and is finished in the usual manner.

The indirect process, while yielding a very good quality of ultramarine, labours under the disadvantages of making it in small quantities only at a time, and of being attended with a large loss of material in the operations.

The Direct Process of Ultramarine-making.—The disadvantages of the indirect method induced the manufacturers to seek a new method, by which larger quantities could be made at one time, and in which the loss of material would not be so great; the labours of the chemists who have been engaged on this object were rewarded with success by the discovery of a direct method having the desired advantages. The direct method can, however, only be used for making the soda ultramarine, but as this happens to be the principal variety, the one disadvantage attending the process is practically of no moment.

The direct process can be carried out either in (1) muffle furnaces, or (2) in crucibles.

1. *Muffle Method.*—A mixture of kaolin, sodium carbonate, sodium sulphate, sulphur, sand, rosin, or charcoal is made, the proportions varying in different works, but approximating to those already given.

The mixture, reduced to the finest state so as to ensure the most intimate union of the ingredients, is placed in layers of from $2\frac{1}{2}$ to 3 inches thick, and firmly pressed down on the floor of the muffle; a charge weighs about 45 lbs. The surface of the charge is covered with fireclay tiles, and the spaces between these luted with mortar; at the front of the muffle one of the tiles is left loose, so that, when required, it can be raised to admit of samples being withdrawn for testing. The front opening of the muffle is now made up, a small aperture being left for the purpose of observing the temperature of the muffle and for drawing out samples from time to time.

The furnace is now heated, at first slowly, towards the last more strongly, so that in about 8 or 9 hours it has attained a dull red heat, at which temperature it is maintained for 24 hours, and then raised to a bright red heat until the end of the operation.

A sample is now withdrawn from the furnace through the hole in the door and a corresponding hole in the tiles; this sample is placed between two tiles as quickly as possible, and a second sample is taken out and placed on the top of the tiles; when the samples have cooled, the colour of the samples are compared. If the operation is finished, the colour of the second

exposed sample will be of the blue colour, while that of the first sample (the covered one) will be of a blue-green colour; when this is found to be the case, the fires are drawn and the furnace and its contents allowed to cool down, care being taken that no air enters into the furnace; or, to make quite sure, the heat is usually maintained for another hour. Should the trial samples have a brown colour, the mass has been insufficiently heated, and the temperature of the furnace is raised a little higher.

When the furnace is opened the ultramarine is found to be in two layers—an upper one of a bright blue colour, and a lower one of a bluish-green; these are separated and finished in the usual way, the upper layer forming the best and the lower layer an inferior quality of ultramarine.

Although the quality of the blue produced by this method is good, yet the quantity capable of being produced is small; therefore it is not much used, and the crucible method described below has replaced it to a large extent.

2. *Crucible Method.*—The method most largely employed for the production of ultramarine is that known as the crucible method, and is carried out as follows:—

A mixture is made of

Kaolin,	100 parts.
Sodium carbonate,	90 "
Sulphur,	110 "
Charcoal,	20 "

A variable quantity of infusorial earth (from 20 to 30 parts) are added, according as the ultramarine has to be rich or poor in silica; in some works 6 parts of rosin are added. All these ingredients are ground together into a homogeneous mass; this is a point of great importance. The mixture is loosely packed into crucibles fitted with flat lids, which are luted on by means of mortar. When the mortar luting is dry the crucibles are piled in ovens large enough to hold from 400 to 500 crucibles, and, in shape, not unlike that described for the first stage of the indirect process. After all doors and openings into the oven are made up it is fired to a bright red heat for several hours, the length of time varying considerably and depending upon a number of factors, such as the state of the weather, the composition of the mixture, &c. Experience is the only school in which an ultramarine-maker can learn how to regulate the time required.

After the heating, all apertures are carefully closed, so as to exclude air, and the furnace allowed to cool for four or five days; the oven is then opened, the crucibles withdrawn and opened,

the contents turned out, and the badly-burnt pieces carefully separated; the good portions are ready to be finished.

The changes which go on during the heating of the mixture are both curious and interesting. The mixture when first put into the crucibles is of a greyish colour, but during the process of burning it passes through quite a series of colour-changes—brown, green, blue, violet, red, and white. The brown appears with the blue flames, due to the burning of the sulphur; it is a fine chocolate brown, but is very unstable; on exposure to the air it enters into combustion. Many efforts have been made to preserve it, but these have been fruitless. The green, which is the next change, begins to form when the sulphur has ceased to burn; like the brown it is unstable, as the substance burns on exposure to the air. Following the green comes the blue, which is formed when the temperature has reached about 700° C., or a bright red heat; when the temperature gets higher the colour changes to a violet. With still higher temperatures, first a red, then a white variety is formed. These changes are due to oxidation; when the white ultramarine is heated with reducing agents, such as carbon, the colours are re-formed in the reverse order to that in which they first appeared.

The form of furnace to be used in burning the ultramarine is not a matter of importance, the operation can be effected in a reverberatory furnace, in a muffle furnace, in earthenware pots, in ovens, or in any convenient apparatus.

Finishing Ultramarine.—By whatever process the pigment is prepared it comes from the furnaces in the form of a gritty, somewhat cindery-looking, blue mass containing a large quantity of soluble sodium salts, and in this condition is unserviceable for use as a pigment. To fit it for this purpose the crude ultramarine has to undergo a finishing process, which has for its object to purify the colour and to develop the hidden beauty of the pigment. The process of finishing is essentially one of washing and levigation. The crude ultramarine is thrown into grinding mills where it is ground with water, this grinding being done as thoroughly as possible, as on it depends to a very large extent the excellence of the pigment as regards colouring power and fineness. After the grinding, the wet ultramarine is run into large tubs, where it is treated with hot water, or even boiled with water, so as to make sure that all the soluble contents of the crude ultramarine are dissolved out. The ultramarine is now allowed to settle and the liquor run off; this contains sodium sulphate which may be recovered by evaporation and used in making new batches of ultramarine. Then clean water is again

run on to the pigment, which, after being thoroughly stirred up, is again allowed to settle and the water again poured off; this washing is repeated several times.

The wet ultramarine is now ground in grinding mills specially constructed for grinding wet materials very finely; such mills will be found described in another Chapter. This grinding is important and takes several hours; the length of time depends upon the use to which the ultramarine is to be put. The finer qualities, which are used in calico-printing and letterpress and lithographic printing, and must be very fine, require the longer grinding; they are sold under the name of calico-printers' ultramarine; painters do not require so fine a quality, and for this the wet ultramarine is not subjected to lengthy grinding. Another method of separating the different qualities of ultramarine is by levigation, which forms an essential part of the process.

The wet ultramarine as it comes from the grinding mills is run into large tubs of water, in which it is thoroughly stirred and then allowed to settle for two hours; this allows the coarser particles to subside, while the finer particles still remain in suspension, and are run into other tubs, where they are allowed to settle. The coarse particles in the first tub are run into the mills again to be re-ground with another batch of crude ultramarine. The particles which settle in the second tubs are collected, dried at a gentle heat, and sent into the market. In the water of the second tub there still remains some fine ultramarine; this is run into a third tub, where it is allowed to settle, and, after drying, is sold as a fine quality. Frequently, there still remains in the last waters some very fine ultramarine, even when the tubs have been allowed to stand for a month to settle; by adding a little lime water, which causes an aggregation of the particles, this can be collected by filtering.

Before being sold the dry ultramarine is, in many works, subjected to a process of sieving, which separates the coarser particles and yields the pigment in the form of an impalpable powder; the finer qualities should have a buttery feel when rubbed between the fingers.

The shade of the finished ultramarine depends upon several factors, such as the proportions of the constituents used in the mixings, the perfection of the burning operations, and the fineness to which the pigment has been ground; as it is impossible to regulate each of these factors with mathematical accuracy, it follows that the shade of the finished colour must vary from time to time; and as this variation is objectionable the makers overcome it by having a number of standard or type colours or

shades, to which standard they bring up all batches by a process of blending and mixing different shades together so as to obtain the marketable brands.

Wet Methods of Making Ultramarine.—Many attempts have been made to prepare ultramarine by wet processes, but mostly without any success. Knapp's process, given in the *Jour. für Praktisch. Chem.*, 1885, p. 375, consists in first roasting a mixture of kaolin, sodium carbonate, and sulphur to such a temperature that the roasted mass has a brown colour, at which point it is maintained until the kaolin is completely decomposed; after cooling, the mass is digested in a solution of sodium persulphide. The defect of this process consists in the small margin there is between success and failure; if the colour of the roasted mass be allowed to pass beyond the brown, the colour of the finished ultramarine begins to deteriorate; and if it becomes red, then no blue is produced when the mass is digested with the persulphide under these conditions the process can hardly become a commercial success.

The colour of the finished product is not quite equal to that of ultramarine made by the dry methods; it is, however, not much inferior.

PROPERTIES OF ULTRAMARINE.—Ultramarine is one of the most important pigments at the command of the painter. As a pigment it is perfectly permanent when exposed under all ordinary conditions, being perfectly fast to light and air, the only destructive agents being acid vapours which rapidly decolorise it. It can be mixed with all the ordinary vehicles used by painters and with most other pigments without being changed thereby or itself causing any change. The only exceptions are those pigments containing lead or copper, which, owing to their forming black sulphides with sulphur, are liable to become discoloured when mixed with ultramarine; the rate of change of such mixtures as ultramarine with chrome-yellow or emerald-green is very variable; sometimes the mixture will change colour very soon, at other times the mixture will keep its colour for a considerable time; much depends upon the quality of the pigments and the care with which they have been made.

Ultramarine is distinguished by its pale but pure tone and by its tint of blue being quite different from that of all other blue pigments. The soda ultramarines are of a violet-blue shade, the variety rich in silica having the darkest and deepest tint; the sulphate ultramarine is of a pale greenish-blue tint and is the palest blue pigment made, resembling blue verditer in tint.

The most characteristic property of ultramarines is their being

readily acted upon by acids; the colour is discharged and the pigment decomposed, sulphuretted hydrogen being evolved and sulphur deposited. All acids have this property, even weak organic acids, such as acetic acid, tartaric acid, &c., this distinguishes ultramarine from all other blue pigments; on the other hand, it prevents the use of ultramarine wherever there is the least chance of its coming into contact with acid influences, which are, sooner or later, sure to destroy the colour. Of the varieties of ultramarine, the sulphate is the most readily decomposed, while the highly silicated soda variety is the most stable of the soda ultramarines. Boiled in strong nitric acid, there is, first, a decoloration, and then a deposition of sulphur; afterwards the sulphur is dissolved and a residue of gelatinous silica is left behind. Alkalies have no action on ultramarine. When boiled in alum, ultramarines take a more violet tone; the sulphate variety is the most readily changed, while the highly silicated soda ultramarine resists the action most; the latter variety is therefore used by papermakers, because, owing to their having to use alum or sulphate of alumina in sizing their papers, they require an ultramarine which will not change much, if anything, under the influence of those bodies. Heat has no action on ultramarine.

COMPOSITION OF ULTRAMARINE.—Ultramarines are compounds of silica, SiO_2 , alumina, Al_2O_3 , soda, Na_2O , sulphur, S, and sulphur oxide, SO_3 . The last, although present in almost every sample of ultramarine, is not an essential constituent of the colour.

The following are some analyses of ultramarines, mostly by the author, which will show the average composition of these important pigments:—

ANALYSES OF ULTRAMARINES.

	Sulphate.	Soap-makers'	Calico-Printers'.	Paper-makers'.	Green.
Silica, SiO_2 ,	49·685	40·647	40·885	45·420	38·52
Alumina, Al_2O_3 ,	23·000	25·047	24·110	21·147	28·94
Sulphur, S,	9·234	12·953	13·740	11·624	8·30
Sulphur trioxide, SO_3 ,	2·464	4·814	3·047	5·578	...
Soda, Na_2O ,	12·492	14·264	15·618	9·906	23·68
Water, H_2O ,	3·125	2·275	2·600	6·325	...
	100·000	100·000	100·000	100·000	99·44

The soap-makers', calico-printers', and paper-makers' ultramarines are of English make, the others of Continental make. The analyses of paper-makers' and soap-makers' ultramarines show the difference between the two varieties of soda ultramarines; the first named is rich in silica, while the other is poor in silica; the soap-makers' and calico-printers' samples are evidently identical in composition, but the latter is much finer than the former. The analysis of green ultramarine shows the difference between the green and blue ultramarines.

CONSTITUTION OF ULTRAMARINE.—One of the problems chemists have endeavoured to solve has been how the various constituents of ultramarine are combined together, but it is still unsolved, and will probably remain so for some time to come; the difficulty of solving it seems to be the inability to effect the substitution of particular groups of elements in it in the same manner as can be done in organic chemistry, where, even in complex molecules, the power of replacing one group by another enables one to form some conception as to the actual constitution of the compound. It is true that the sodium in ultramarine can be replaced by silver and other metals so as to form varieties of ultramarine, and that the sulphur can be replaced by selenium or tellurium; but these replacements throw no light on the problem, for they are simply replacements of one element by another, not of groups of elements.

Many chemists, *e.g.*, Wilkins, Hofmann, Unger, Endeman, and Elmer, have worked on this question.

Hofmann's theory of the constitution of ultramarine is, perhaps, nearest the truth. Hofmann was head of the Marienberg Ultramarine Works and did much to throw light on this subject; he considered ultramarine to be a double silicate of alumina and soda combined with bisulphide of sodium. The formula assigned to the soda ultramarine poor in silica was $4(\text{Al}_2\text{Na}_2\text{Si}_2\text{O}_8) + \text{Na}_2\text{S}_4$, and to that rich in silica, $2(\text{Al}_2\text{Na}_2\text{Si}_3\text{O}_{10}) + \text{Na}_2\text{S}_4$.

Endeman considers that the ultramarines contain a colour-nucleus (an oxysulphide of alumina and soda) disseminated through a double silicate of alumina and soda.

The colour-nucleus of white ultramarine (which may be regarded as the parent body) has the formula $\text{AlNa}_4\text{O}_2\text{S}_2$; the action of sulphur upon this is to remove soda and to form green ultramarine, which contains the nucleus, $\text{Al}_2\text{Na}_2\text{S}_2\text{O}_3$; this, by oxidation, can be converted into $\text{Al}_2\text{Na}_4\text{S}_3\text{O}_3$ which has a jet green colour; by burning with sulphur, this is converted into the nucleus of the blue variety, which has the formula $\text{Al}_2\text{Na}_2\text{S}_3\text{O}_3$. The base through which the colour-nucleus is distributed is of

variable composition; Endeman gives the formula of one variety as $16 \text{ Si O}_2, 3 \text{ Al}_2 \text{ O}_3, 5 \text{ Na}_2 \text{ O}$. But all this is open to great doubt.

The most competent authorities consider that the green ultramarine is not a true chemical compound, but a combination of the blue with sodium salts; because, by simply boiling with water, it is converted into the blue ultramarine, while soluble sodium salts are found in the water; on the other hand, by heating the blue ultramarine with sodium sulphate and charcoal, it is converted into the green ultramarine.

Gueckelberger, one of the most recent writers on the subject, confirms the figures given by Hofmann; but considers that the ultramarines are derived from a typical compound containing Si_{18} ; thus, for the variety rich in silica he proposes the formula $\text{Si}_{18} \text{ Al}_{12} \text{ Na}_{20} \text{ S}_6 \text{ O}_{62}$; while the variety poor in silica has the formula $\text{Si}_{18} \text{ Al}_{18} \text{ Na}_{20} \text{ S}_6 \text{ O}_{71}$. It is doubtful whether ultramarines have the complex composition here assigned to them and, moreover, no light is thrown on their constitution.

ASSAY AND ANALYSIS.—As there is so much difference between various makes of ultramarines, it is necessary to assay for colour, fineness, body, &c. Those ultramarines which are to be used by paper-makers should be tested for their power of resisting the action of alum; this can be done by taking about 5 grammes and boiling in a solution of alum of about 5 per cent. strength. To see what change of colour may have taken place, 5 grammes of the colour should be shaken up with clean water and the two wet samples compared together; any change brought about by the alum can then be readily detected.

It is rarely that a complete analysis of ultramarine is required; in such an event, the following scheme can be adopted:—

For Water.—Heat 2 grammes in a weighed crucible for about half an hour over the Bunsen flame; the loss in weight is the amount of water present.

For Silica, Si O_2 .—Treat 2 grammes with hydrochloric acid until the colour is completely destroyed; evaporate the mixture to dryness and gently ignite the residue; treat the dry mass with hydrochloric acid, filter off the insoluble silica, well wash it, then dry, and burn in a weighed crucible; the increase in weight *minus* the weight of the filter-paper ash is the weight of the silica.

For Alumina, $\text{Al}_2 \text{ O}_3$.—To the filtrate from the silica add ammonia in slight excess, boil gently, then filter, and treat the precipitate of alumina as the silica.

For Soda, $\text{Na}_2 \text{ O}$.—To the ammoniacal filtrate from the alumina add sufficient sulphuric acid to neutralise the ammonia, then evaporate to dryness in a weighed basin and ignite the residue



until all ammoniacal fumes have been given off; weigh the residue of sodium sulphate, and multiply this weight by 0.4366 to ascertain the weight of the soda, Na_2O .

Total Sulphur.—Treat 2 grammes of the ultramarine with a mixture of 2 parts of nitric acid and 1 part of hydrochloric acid, until the colour is completely decomposed and only a transparent mass of silicate is left; filter this off, and to the filtrate add a solution of barium chloride in excess, boil and filter, wash the precipitate well, dry, burn, and weigh it in a crucible. To find the weight of sulphur, multiply the weight of barium sulphate so found by 0.13734; from this deduct the weight of sulphur present as sulphuric acid to find the quantity of sulphur present as sulphide.

For Sulphur as Sulphuric Acid.—Weigh out 2 grammes of ultramarine, treat with dilute hydrochloric acid, filter off the precipitated sulphur and silica, and precipitate the filtrate with barium chloride, treat the precipitate as in the last. To find the amount of sulphur trioxide present, multiply the weight of the barium sulphate so found by 0.34335.

ULTRAMARINE DERIVATIVES.—It has been stated above that some of the constituents of the blue and green ultramarines can be substituted by other analogous bodies, such as selenium for the sulphur or the sodium by silver; in this way other ultramarines can be prepared, but, as a rule, they are only of scientific interest, as their colour is of no technical moment, as will be seen later on; hence they are not made on a large scale; still their production may ultimately throw light upon the question of the chemical constitution of ultramarine, and the fact of their formation must be faced by all chemists who essay to deal with this question. There are one or two coloured derivatives of ultramarine which are used to a limited extent; these are the violet and red ultramarines.

VIOLET ULTRAMARINE.—This product can be made from either the green or blue ultramarines, from which it differs by containing less sulphur and more alumina. It can be made in several ways. Zeltner makes violet ultramarine by submitting either the blue or green varieties to the temperature of about 300°C ., and passing chlorine gas over them; at first the colour is, if the blue is used, turned green, then this becomes dark red; at this point the operation is stopped and the red product is boiled in an alkaline solution until it turns violet; after which it is washed. Instead of using dry chlorine at a temperature of 300°C ., the green or blue varieties may be heated in a mixed current of steam and chlorine at a temperature of 160° to 180°C .,

until the colour is developed; after which it is washed with water to free it from the sodium chloride formed, and dried.

In another method, devised by Hofmann, blue ultramarine mixed with about 2.5 per cent. of ammonium chloride; the mixture heated to a temperature of 200° C., exposed to the air until the violet colour is properly developed, and the mass allowed to cool slowly; when cold, it is washed thoroughly and dried.

Violet ultramarine has very similar properties to the blue variety, and is similarly decomposed by acids; boiling in alkalis changes the colour to blue. The shade of the pigment is a very pale reddish-violet. This pigment is not used to any great extent owing to its want of colouring power. In composition it resembles the blue varieties; a sample analysed by the author contained:—

Silica, Si O ₂ ,	42.010 per cent.
Alumina, Al ₂ O ₃ ,	26.360 "
Sulphur, S,	9.235 "
Sulphur trioxide, S O ₃ ,	3.140 "
Soda, Na ₂ O,	17.905 "
Water, H ₂ O,	1.350 "
	100.000

RED ULTRAMARINE.—Zeltner prepares the red ultramarine by exposing the blue variety at a temperature of 130° to 150° C. to the action of the vapours of nitric acid, when he obtains deep or dark red, or light rose or pink shades, according as the acid vapours are dilute or strong. Hofmann prepares the red ultramarine by passing dry hydrochloric acid gas over either the blue or violet varieties until the proper colour is developed, when the mass is washed and dried.

OTHER ULTRAMARINES.—By using boracic acid instead of silica a boron ultramarine of a blue colour is obtained. **Yellow ultramarine** is made by heating the blue ultramarine with a solution of silver nitrate, in sealed tubes, at a temperature of 120° C. for 15 hours; the sodium is replaced by silver, and the new pigment contains 46.5 per cent. of silver.

The blue ultramarine heated with silver chloride turns green, taking up silver in the process. The *yellow silver ultramarine* heated with sodium chloride loses some of its silver, turning green; if the sodium chloride is replaced by potassium chloride a *bluish-green potassium ultramarine* is formed. If barium chloride is used a *yellowish-brown barium ultramarine* is obtained; in the same way zinc chloride yields a *violet zinc ultramarine*, and

magnesium chloride a *grey ultramarine*. None of these products have any technical value.

The sulphur can be replaced by selenium, when *brown* and *purple ultramarines* are obtained.

PRUSSIAN BLUE.

Prussian blue, or Berlin blue, or Chinese blue, is, next to ultramarine, the most valuable blue pigment in use for painting and other purposes for which pigments are used. It was discovered in the early part of the last century (about 1704) by a Berlin colour-maker, named Diesbach, by accident, as many such discoveries have been made. Diesbach was making Florentine lake, and for this purpose he used a solution of cochineal, which he mixed with alum and copperas (ferrous sulphate) and precipitated with an alkali; in the particular instance which led to the discovery of Prussian blue he used an alkaline solution (which had been used to purify some Dippel's oil made by distilling ox blood), and instead of getting a red lake he got a blue. Diesbach followed up this discovery and found that the blue could be got by calcining blood with alkali, and, after lixiviating the mass, precipitating the liquor with a solution of copperas.

The technical manufacture of this pigment was further developed by a London colour-maker, named Wilkinson, from whom the colour was named "Wilkinson's blue," a name which is now obsolete. Wilkinson prepared the colour by first deflagrating a mixture of tartar and saltpetre, and calcining the residue with dried blood; the fused mass was lixiviated with water, and to the lye so obtained a solution of alum and copperas was added; the resulting pale blue precipitate was treated with hydrochloric acid to develop the blue.

Since the time of Diesbach and Wilkinson the composition of Prussian blue has been the subject of numerous researches by chemists, so that very little remains to be learnt as to the composition and constitution of this blue.

Prussian blue is a compound of iron, carbon, and nitrogen; the carbon and nitrogen are combined together in the form of the radicle cyanogen, CN , which is the characteristic element of a group of compounds, of which Prussian blue is a member, known as cyanides. The iron exists in the blue in two forms; one in combination with the cyanogen in an acid condition, the other in the basic condition. When Prussian blue is boiled with a solution of potash it yields oxide of iron (which remains as an insoluble red mass), and a yellow solution, which, on being

allowed to crystallise, deposits yellow tabular crystals of a compound of potassium, iron, carbon, and nitrogen, originally known as yellow prussiate of potash; the iron in this exists in combination with the carbon and nitrogen in an acid state, forming the radicle known as ferrocyanogen, $\text{Fe C}_6 \text{N}_6$. The chemical name of the yellow prussiate of potash is potassium ferrocyanide, $\text{K}_4 \text{Fe C}_6 \text{N}_6$. Besides the yellow prussiate there is another, the red prussiate or potassium ferricyanide, $\text{K}_3 \text{Fe C}_6 \text{N}_6$. These two compounds differ from one another in their colour and in the reactions which they give with iron salts. With ferrous salts the ferrocyanide gives a bluish-white precipitate of ferrous ferrocyanide; while with ferric salts a deep blue (Prussian blue) precipitate of ferric ferrocyanide is obtained. With ferrous salts the ferricyanide gives a deep blue precipitate of ferrous ferricyanide (Turnbull's blue); with ferric salts no precipitate is obtained, but the colour of the solution becomes a little darker. The production of Prussian blue is a most characteristic reaction of iron, no other metal is capable of producing it, and very minute traces of iron in a solution can be detected by adding a few drops of a solution of potassium ferrocyanide.

It has been ascertained by various observers that the precipitates obtained by adding solutions of the prussiates to solutions of iron salts contain potassium as an essential part of their composition, and it is difficult, although possible, to rid them of this potassium. Thus the bluish-white precipitate is really potassium ferrous ferrocyanide, $\text{K}_2 \text{Fe C}_6 \text{N}_6$; Prussian blue is potassium ferric ferrocyanide, $\text{K}_2 \text{Fe}_2 \cdot 2 \text{Fe C}_6 \text{N}_6$; Turnbull's blue is potassium ferro-ferricyanide, $\text{K Fe Fe C}_6 \text{N}_6$.

Prussian blue and Turnbull's blue have exactly the same composition, but their constitution is different; the one being a ferrocyanide and the other a ferricyanide. Skraup,* Reindel,† Kekule,‡ and other authorities consider that they are identical; but that they are different is proved by the fact that when the alkali is eliminated from them the residual blues are of different composition, Prussian blue having the composition $\text{Fe}_7 \text{C}_{18} \text{N}_{18}$, and Turnbull's blue the composition $\text{Fe}_3 \text{C}_{12} \text{N}_{12}$ §; then the shade of the two blues is different, Prussian blue is a greenish-blue, while Turnbull's blue is a violet-blue.

COMMERCIAL PRUSSIAN BLUE.—In commerce several varieties of Prussian blue are sold under the names of—

* Skraup, *Liebig's Annalen*, clxxi., p. 371.

† Reindel, *Jour. Prak. Chemie*, cii., p. 38.

‡ Kekule, *Lehrbuch. Organ. Chem.*

§ Williamson, *Mem. Soc. Chem.*, iii., p. 125; Reynolds, *Jour. Chem. Soc.*, li., p. 644.

1, Chinese blue; 2, Prussian blue; 3, soluble blue; 4, Antwerp blue; 5, Brunswick blue, and others of less importance. There are several synonyms, such as Berlin blue and Paris blue. Turnbull's blue is a name rarely met with now. No special distinction is made between a blue obtained from the red prussiate or a blue obtained from the yellow prussiate of potash.

CHINESE BLUE.—This is the name given to the best qualities of Prussian blue, and in the manufacture of which every care is taken to obtain a product of good colour. Chinese blue is especially characterised by being in pieces or powder having a fine bronze lustre, the pieces break with a peculiar conchoidal fracture, and the fractured surfaces show the lustre or bloom; it is completely soluble in oxalic acid. Chinese blue is largely used by calico-printers and dyers. It is a blue of a greenish shade.

Chinese blue is made as follows:—1 cwt. of ferrous sulphate (green copperas), as free from insoluble oxide as possible, is dissolved in cold water, and to it is added 10 lbs. of sulphuric acid. This solution must be made as required, as it soon begins to oxidise, and to deposit oxide of iron, while the liquor will then not make good Chinese blue. One cwt. of yellow prussiate of potash is dissolved in water.

The solutions should be made as dilute as possible, not less than 30 to 35 gallons of water for each cwt. of material; even weaker solutions are preferable, as these yield finer precipitates than strong solutions, and so facilitate the production of the lustre on the finished blue.

On mixing the solutions a bluish-white precipitate is obtained, which is allowed to settle, and the clear liquor poured off; to the residual blue is added—first, a thin cream of 20 lbs. of bleaching powder with water, which is thoroughly mixed with the precipitate, and then some hydrochloric acid, and the blue colour gradually develops. It is allowed to settle, the top liquor run off, and the blue well washed with water, and drained on a filter; the wet mass is then pressed into drying-pans, and slowly dried in the dark, at a temperature not exceeding 120° to 130° F.

It is important that the oxidation of the precipitate first obtained be done by purely chemical means, and not by the agency of the oxygen of the air; in the former case a pure blue colour is obtained, while in the latter case oxide of iron is mixed with the blue, and materially influences the tint of the pigment. The best oxidiser and the cheapest is bleaching powder; nitric acid may be used, but it is more costly and not more efficient than bleaching powder. It will be found best to

add the oxidiser in small quantities, as when used all at once there is generally an escape of chlorine, owing to this body being evolved rather more rapidly than the blue can take it up, which not only increases the cost of production, but also deleteriously affects the workmen's lungs. No part of the blue should be allowed to come in contact with the atmosphere before it is fully oxidised. The slower the colour is dried, the better and finer is the lustre of the finished product.

Instead of adding the bleaching powder after precipitating, it may be added to the iron solution to oxidise that to the ferric condition; the blue obtained is not of so green a tint, being, if anything, a little more violet.

If a blue with a violet tint is required it may be made by dissolving 1 cwt. of copperas in water and adding first 10 lbs. of sulphuric acid, and then a solution of 1 cwt. of the red prussiate of potash. The precipitate is collected, washed with water, and dried as before.

Chinese blue is mostly sold in the form of small cubical lumps, about 1 to 2 inches in diameter, but it is also sold in the form of fine powder. In grinding the blue great precaution is required to exclude particles of iron, as the production of a spark will ignite the dry powdered Chinese or Prussian blue and reduce it to a mass of red oxide of iron.

A sample of Chinese blue examined by the author had the following composition:—

Water,	4·487	per cent.
Oxide of iron,	52·055	„
Cyanogen,	43·508	„
	<hr/>	
	100·000	

PRUSSIAN BLUE.—The commoner makes of blue are sold under the names of Prussian blue, Berlin blue, paste blue, &c., in two forms, dry and pulp or paste. Some makes of these blues have a green shade, and others a violet shade or tint, owing to slight differences in the method of making.

Green-tint Blues.—There are several ways of making these blues. 1. Dissolving 1 cwt. each of yellow prussiate of potash and copperas in about 50 gallons of water, mixing the two solutions, allowing to settle, pouring off the clear top-liquor, washing the colour with water, then throwing it on to the filter and allowing it to be exposed to the air until it has acquired the desired blue; to facilitate this the blue should be turned over from time to time so as to expose fresh surfaces to the action of the air.

This method is not a good one as it leads to the production of oxide of iron in the colour, which affects the shade of the colour; it may be got rid of by treating the wet colour with hydrochloric acid, but this adds to the expense of making.

2. The blue is precipitated as before, but the colour is developed by adding bleaching powder. This process is identical with that used in making Chinese blue, but is less carefully carried out.

3. One cwt. of copperas, 20 lbs. of alum, and 10 lbs. of sulphuric acid are dissolved in water and a solution of 1 cwt. of yellow prussiate of potash added; the mixed solutions are allowed to stand for 2 or 3 hours, when they are finished as in No. 1. The addition of alum makes the shade of blue lighter and, when dry, much easier to grind; the proportion of alum added varies with different makers; at one time comparatively large quantities were added, but the tendency has been of late years to reduce the proportion. When a solution of yellow prussiate is added to one of alum there is no immediate precipitate, but on standing for about an hour a bluish-white precipitate falls down, the nature of which is somewhat uncertain.

In the early days of Prussian-blue making blue-makers usually made their own prussiate, which, owing to the rough mode of preparation, yielded liquors containing a good many impurities, such as cyanides, sulphides, carbonates, and other salts of iron. The use of this crude liquor necessitated the use of much acid to prevent them from precipitating the iron in other forms than Prussian blue; as the makers objected to the use of much acid they added alum instead, but, as a result, they got a paler blue. Blue makers rarely use such crude leys now, as the refined crystal prussiate is cheap and makes better blues with less trouble.

Violet-tint Blues.—These are sometimes known as Paris blue. They are made by dissolving 1 cwt. each of the red prussiate of potash and copperas in water, adding the two solutions together, allowing the precipitated blue to settle, pouring off the top-liquor, washing the residue with water, filtering, and drying the blue.

When sold as pulp blues or paste blues the blue is simply allowed to drain on the filter and not dried; such pulp colours contain from 25 to 30 per cent. of dry colour, as a general rule, although as little as 17 per cent. has been found in some makes; such pulp colours should always be bought under a guarantee of the quantity of actual dry colour they contain.

SOLUBLE BLUE.—While Chinese and Prussian blues are ordinarily insoluble in water and acids, yet a variety of the blue

can be made which is soluble in water; so far as chemical composition is concerned this soluble blue does not differ from the insoluble varieties. Many recipes have been published for its preparation, of which the following are the principal:—

1. Prepare a solution of 100 lbs. of perchloride of iron and 10 lbs. of Glauber's salt. A solution of 217 lbs. of yellow prussiate of potash and 10 lbs. of Glauber's salt is also prepared. The iron solution is poured into the prussiate solution, whereby a blue precipitate is obtained; this is collected on a filter and washed with water until the wash-waters are tinged with blue; it is then dried. In making soluble blue in this way it is important to pour the iron solution into the potash solution, and to keep the latter in excess. The object of adding the Glauber's salts is to ensure the complete precipitation of the blue by taking advantage of the fact that, while soluble in water, it is not soluble in saline solutions, so that by having the liquor saline there is a more complete precipitation of the blue.

2. Dissolve 72 lbs. of copperas in hot water, and pour this solution into a hot solution of 110 lbs. of red prussiate of potash, and boil the mixture for two hours, filter, wash until the wash-waters have a blue colour, then dry the residual blue.

3. Take 100 lbs. of Prussian blue, mix well with about 100 gallons of water, and add 50 lbs. of yellow prussiate of potash, boil well for 3 to 4 hours, drain on a filter, wash as before, and dry.

4. Dissolve separately in water 100 lbs. of yellow prussiate of potash, and 80 lbs. of copperas, add the two solutions together, and boil for 1 hour; then add 20 lbs. of nitric acid and 10 lbs. of sulphuric acid, and boil 1 hour longer; then filter, wash, and dry as before.

Soluble blue is not made on so large a scale now as formerly. It is used mostly for making blue ink and for painting velvets, for which purposes it has been replaced by the aniline blues.

ANTWERP BLUE.—This blue has practically gone out of use, its place having been taken by the Brunswick blue described below. Antwerp blue is made as follows:—20 lbs. of copperas, 10 lbs. of alum, and 10 lbs. of zinc sulphate are dissolved in 50 to 60 gallons of water, and to this solution is added one of 40 lbs. of the red or yellow prussiate of potash, dissolved in 50 to 60 gallons of water. The blue is finished in the ordinary way.

Antwerp blue is paler in colour than Prussian blue, and is probably a mixture of the ferrocyanides of iron, zinc, and alumina. Its properties are almost identical with those of Prussian blue.

BRUNSWICK BLUE.—Brunswick blue is a pigment of quite a recent origin, but it is now very largely made and used by painters. Essentially it is a mixture of Prussian blue and barytes, although some makers add other ingredients, as will be noted below.

It is made in several shades—deep, medium, and pale. The deep shade is made by thoroughly mixing 1 cwt. of barytes with 50 to 60 gallons of water, adding a solution of 5 lbs. of copperas, then a solution of 5 lbs. of either the red or yellow prussiate of potash, taking care that the mass be kept well stirred during the whole time of mixing, so as to ensure the thorough incorporation of the barytes with the blue. After filtering, washing, and drying the blue is ready for use. For a medium shade the same quantity of barytes is used, but only 3 lbs. of each of the other ingredients. The pale shade is made with 1 lb. of the iron and potash salts to 1 cwt. of barytes. Some makers add a little ultramarine to the blue.

Instead of barytes gypsum may be used, in which case the quantities of iron and potash salts must be increased by one-half, while china clay requires double the quantities to give blues of equal depth of colour.

A sample of Brunswick blue analysed by the author had the following composition :—

Water,	275	per cent.
Alumina, Al_2O_3 ,	2.450	„
Ferric oxide, Fe_2O_3 ,	3.310	„
Barytes and silica,	89.860	„
Cyanogen and sulphur,	4.105	„
		<hr/>	
		100.000	

This sample contained both Prussian blue and ultramarine, in the proportion of about 7 per cent. of the former and 5 per cent. of the latter.

Brunswick blue is a very good pigment, is permanent, and not readily affected by exposure to air, light, &c. It is subject to one defect, viz., that when mixed with oil and turps into a paint the white portion is apt, on standing, to settle down, leaving the blue suspended in the liquid; thus, in common parlance, the blue comes to the top; this is easily remedied by giving the paint a stir before using.

PROPERTIES OF PRUSSIAN BLUES.—Prussian blues are characterised by their deep greenish-blue tint; there is no other blue of the same depth of colour or of the same shade or tint. When dry, they have a bronzy appearance, which is

greatest when the blue is pure, and is specially characteristic of the variety known as Chinese blue.

They are very hard and exceedingly difficult to grind, and for Prussian blue to develop its full colouring powers it is essential that it be ground as fine as possible; it is partly on account of this difficulty of grinding that Brunswick blue has come so largely into use, as painters are saved the trouble of grinding.

Prussian blue is insoluble in dilute acids and, usually, in strong hydrochloric acid (see below); boiling with nitric acid turns it of a greenish shade; while when boiled with strong sulphuric acid it is decomposed, sulphate of iron being formed, and hydrochloric acid, &c., evolved. Some samples are insoluble in strong hydrochloric acid, others are soluble; much depends upon the process used in making and also upon the age of the sample; keeping seems to bring about some changes in the blue, whereby it is less easily soluble in the various agents which dissolve freshly-prepared blue readily enough.

Oxalic acid dissolves Prussian blue very readily; one part of oxalic acid will dissolve six parts of blue; such solutions have been used to make blue inks, but since the aniline colours came into commerce the use of Prussian blue for ink-making has decreased. By digesting the ordinary Prussian blue with a saturated solution of oxalic acid at the ordinary temperature, it is slowly converted into the soluble variety; on the other hand, if a solution in oxalic acid is boiled, the blue is gradually precipitated in the ordinary form; the same result can be brought about by the addition of sulphuric acid.

The most characteristic reaction of Prussian blue, which serves to distinguish it from other blues, is that when treated with any alkali, such as soda, potash, ammonia, or lime, it is decomposed into a ferrocyanide of the alkali and oxide of iron, the last being left behind as an insoluble residue having a red-brown colour, while the former passes into solution. Addition of acid in sufficient amount restores the blue colour, provided the ferrocyanide of the alkali formed has not been washed away. The Prussian blues and the pigments containing it cannot be used with alkaline vehicles, such as lime, whiting, silicate of soda, or silicate of potash, because the blue would thereby be changed to red.

As a pigment Prussian blue is quite permanent and resists exposure to air, light, and most of the other atmospheric influences which act on pigments; it has, however, one curious property, that of fading a little on exposure to light and of recovering its original intensity of colour in the absence of light.

Its colouring powers are very great, being by far the best of all the blues in this respect; it is rather a transparent colour, so that its covering power is not great.

Heat decomposes it; the cyanogen it contains burns off as carbonic acid and nitrogen, while a blackish-brown or reddish-brown residue is left behind, according to the temperature to which it is exposed; a low temperature does not completely decompose it, and so a blackish-brown residue, consisting of a mixture of oxide of iron and carbon, is left behind; on the other hand, a high temperature causes all the carbon to be burnt off and a reddish-brown residue of ferric oxide to be left behind. In some cases this last residue may be a mixture of the two oxides of iron, ferrous and ferric, or it may be a mixture of ferric oxide and metallic iron; the result depends upon the conditions under which blue is heated and its purity. The proportion of residue left depends upon the state of dryness of the blue, the process used in making it, and its purity; good qualities leave from 40 to 50 per cent. of residue.

Prussian blues can be mixed with nearly all other pigments without being affected or changed by them or affecting them in any way; the only exceptions are the few pigments of an alkaline character which destroy Prussian blue in the manner above described.

ASSAY AND ANALYSIS OF PRUSSIAN BLUES.—

Prussian blues can be assayed for colouring power and tint by the usual methods. The paste blues should be assayed for the amount of actual colour they contain by taking a known weight and heating in a drying oven at from 120° to 130° F. for some hours; the loss in weight represents the amount of water present, and the difference is the amount of solid matter or dry colour.

An analysis of Prussian blues is rarely required. When required, the blue should be boiled with ammonia until the blue colour is completely decomposed; filter off the residue; the filtrate contains ammonium ferrocyanide and any zinc and magnesia which may be present. The two latter bodies can be tested for by the usual methods. The residue should be thoroughly well washed with water to free it from all traces of alkali; after which, it is treated with hydrochloric acid, when, if pure, it will all dissolve; if there is a white residue it may be barytes or gypsum or china clay, which may be detected by the application of special tests. The solution will contain iron and alumina, and may be examined for these by the usual chemical methods.

If the amount of Prussian blue in Brunswick blues (or other blues made by diluting Prussian blue with a white pigment) is

required, a known weight of the sample should be boiled in caustic soda until the blue is completely decomposed; the mixture is then filtered and the brown residue well washed with hot water until it is quite free from alkali; next it is treated with hydrochloric acid until the brown oxide of iron has been dissolved; lastly, it is filtered, and to the filtrate is added ammonia in slight excess; the precipitate of oxide of iron thus formed is filtered off, washed with water, dried, and burnt in a crucible, and then weighed. The weight of the oxide of iron multiplied by 2.212 gives the amount of Prussian blue in the sample taken.

To detect Prussian blue in admixture with other pigments a portion should be boiled with caustic soda, when it will become brownish-red or change in shade, according to the character of the mixture and the amount of Prussian blue present. To further confirm the presence of Prussian blue the alkaline mixture should be filtered and to the filtrate as much hydrochloric acid be added as will neutralise the alkali and then a little ferric chloride; if Prussian blue be present, a blue precipitate will be obtained.

COBALT BLUES.

Cobalt is a metal characterised by the fine blue colour of some of its compounds, notably those with alumina, silica, and phosphoric acid; all these have a fine violet-blue tint, and, being very insoluble bodies and unaffected by most destructive agencies, they have been used to a greater or less extent as pigments.

There are two commercial forms of cobalt blue. The one, smalts, which is really a glass coloured by cobalt, was largely used before it gave place to artificial ultramarine. The other, known as cobalt blue, is a compound of cobalt, alumina and, occasionally, phosphoric acid; it has a fine pale blue tint and is mostly used by artists.

SMALTS.—Smalts has been used as a pigment for a very long period, although, of late years, its use has considerably declined owing to its tint being impaired by gas light, its weak colouring power, and its great inferiority to the much cheaper artificial ultramarine.

Manufacture of Smalts.—The manufacture of smalts takes place in three stages—1st, the preparation and roasting of the cobalt ore; 2nd, the preparation of the blue glass; 3rd, the grinding and levigation of the glass to form the smalts.

1st Stage—Preparation, &c., of the Ore.—The ores of cobalt most used in the preparation of smalts are three in number—viz.,

cobalt pyrites, Co_2S_3 , so called because it resembles the common iron pyrites in appearance; smaltine, Co As_2 ; and cobalt glance, $\text{Co}_2\text{As}_2\text{S}_2$. These ores rarely occur quite pure, but are mostly found mixed with small quantities of other metals, such as iron, nickel, antimony, bismuth, and with earthy impurities; these have to be separated before the ore can be used for the manufacture of smalts, as many of them have an injurious effect on the tint of the finished article. This removal is effected in two ways—1st, by hand-picking the ore; 2nd, by roasting the picked ore. The ore is carefully picked over by hand so as to remove the larger impurities; the picked ore is next ground as fine as possible under edge-runners or stamps, and the lighter and more earthy particles removed by levigation, so as to leave a washed ore containing a large proportion of cobalt. This washed ore is then dried and placed in charges of about 3 to 5 cwts. on the hearth of a reverberatory furnace, where it is subjected to a slight roasting or oxidation. This reverberatory furnace is constructed in a special manner; the cobalt ores used contain a large amount of arsenic which is converted in the furnace into arsenious oxide. This oxide, being volatile, passes into the flues, which are arranged in long spirals round the furnace, so as to ensure its complete condensation, and thereby prevent any of this dangerous ingredient escaping into the air. The flues are cleaned out from time to time, for which purpose doors are made in the sides of the furnace communicating with different parts of the flue as shown in Fig. 22. This figure is a plan of a cobalt ore roasting furnace, where A is the bed or hearth of the furnace; B the fireplace; C, C, C, C are the various parts of the flue; D, D, D, D are doors communicating with the flue, through which the flue is cleaned out when required. The flue is only partly shown, as it winds round the furnace more than once.

The roasting of the ore in this furnace causes the arsenic to become oxidised to arsenious oxide, As_2O_3 , which is so completely volatilised that the roasted ore rarely contains any arsenic; the sulphur in the ore is burnt to sulphur dioxide, S O_2 , which passes into the chimney; while the metals are converted into oxides. This roasted ore is sold, under the name of *zaffre*, for colouring glass and pottery. For smalts-making it is found best not to roast the ore to the full extent, but to leave a little of the arsenic and sulphur in it; the object of this is to ensure that in the next stage of smalts-making, all the impurities are removed. Cobalt has a great affinity for oxygen and but little for arsenic or sulphur; whereas nickel and copper have great affinity for these elements; so that when the roasted ore is melted with alkalis,

the copper and nickel with the iron, sulphur and arsenic combine together and form what is called a *speiss* or *regulus*, which collects under the glass; when bismuth and antimony occur in the ore, they are partly liquated out before the actual roasting, and the rest passes into the regulus.

The percentage of cobalt in the roasted ore varies so con-

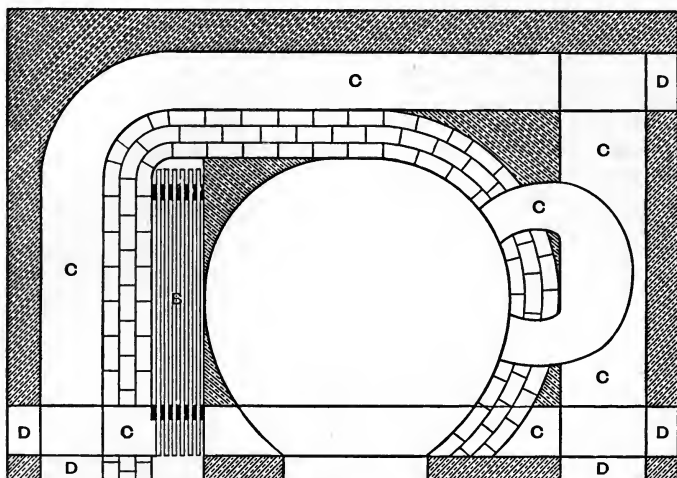


Fig. 22.—Cobalt ore roasting furnace.

siderably that no definite instructions for smalts-making can be given in text-books; the quantities of materials used depend upon the strength of the zaffre, as will be noted below.

2nd Stage—Preparation of the Blue Glass.—The roasted ore is now mixed with silica and potash and melted in a furnace, when the cobalt, silica, and potash combine together to form a blue glass. The potash used must be of the best quality and as free from impurities as possible; soda, in particular, should be avoided, as its influence on the tint is bad; iron and other metals should also be absent. The silica is used in the form of quartz, and is purified by hand picking, so as to have it as free as possible from lime, alumina, and ferruginous impurities, as these cause the tint of the glass to be very dull. The quartz is ground as finely as possible under edge-runners, and the various ingredients are carefully and thoroughly mixed together in wooden tubs, the use of metal being avoided for fear of any getting among the mixture.

Sometimes a little white arsenic is added so as to ensure that any iron which may be in the mixture shall find its way into the regulus.

The proportions of zaffre, silica, and potash used varies according to the strength of the zaffre (which is the actual colouring agent) and to the depth of colour required in the finished product; usually the amount of potash is kept at a fixed quantity—viz., one-third the total weight of the ore and quartz combined. The actual proportions used are always determined by a trial on a small scale with every fresh batch of zaffre, and from the depth of colour of the glass thus obtained the manufacturer judges as to the proportions needed on the large scale to produce the shade of smalts required. The various ingredients are carefully weighed out and thoroughly mixed (as noted above); too much care cannot be taken on this point, as upon it depends much of the success of the operation.

The materials are now placed in earthen crucibles made of as strongly a refractive clay as can be obtained; these crucibles must not contain any lime. They are usually about 18 inches in diameter at the top and about 14 inches at the bottom; they hold about 84 lbs. of material. They last for from six to seven months.

The furnace in which these pots are heated is similar in construction to a glass furnace, although other forms may be used.

A German smalts furnace is shown in Fig. 23, where A A are two of the pots, and B an opening through which the pots are placed in the furnace; there are several of these openings placed round the furnace. After the pots have been placed in position the openings are bricked up, a hole being left for the purpose of removing the speiss, the glass, &c. These openings are kept closed up during the time the melting is proceeding. Above the openings, B, are small ones through which the materials in the crucible are worked and through which the blue glass is removed at the end of the operation. E is the fireplace. F F are flues in the roof of the furnace communicating with the chimneys, G G.

The pots, after they have been placed in the furnace and all openings (except the working ones) have been closed up, are charged with material by means of iron ladles, and the fire lighted. In about 8 hours the material begins to fuse or melt; it is then thoroughly stirred and the temperature raised to a white heat, when the glass begins to form. When the mass has become quite homogeneous (which is ascertained by taking small samples from time to time from the pots) and it is seen that the speiss has settled out, the glass is ladled out into cold water and the speiss drawn off from the bottom of the pots by the holes

which have been made for that purpose; after which the pots are re-charged for another lot, which is done through the hole at the top of the furnace-opening, B. The object of throwing the glass into cold water is to break it up into small pieces so as to facilitate the grinding.

3rd Stage—Grinding.—The blue glass thus obtained is in angular fragments of about an inch in size, which are ground and levigated to form the smalts. The grinding is done very thoroughly, so as to have the material as fine as possible. In some works the first or rough grinding is done under stamps; then the rough material is further ground to the required degree

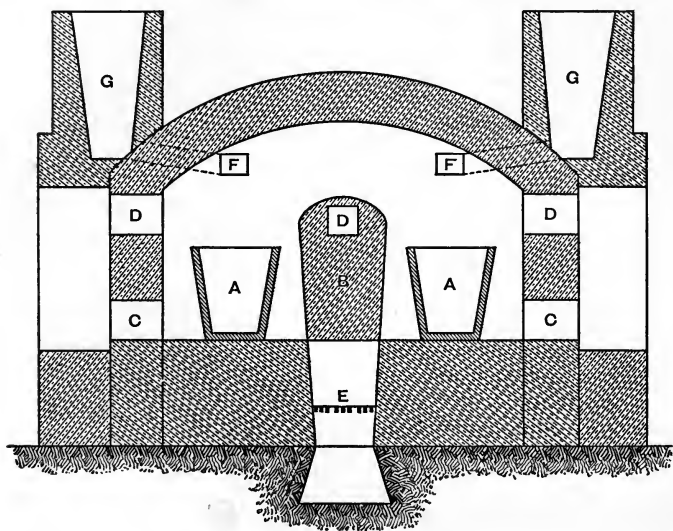


Fig. 23.—Smalts furnace.

of fineness under edge-runners with water; or, if required, the whole grinding may be done with a set of edge-runner mills. After some hours grinding, the mass of ground material is sent into a series of settling tanks, in the first of which the coarsest particles settle, but, being too coarse for use, these are sent through the edge-runners again; in the next tanks the smalts collects; this is taken out of the tanks, dried, and sent into the market. The fine material which settles out in the last tank of the series is usually of too pale a colour to be of use, and the maker generally returns it to the crucible to be remelted.

Five tons of glass yields about 3 tons of smalts; the loss of 2 tons is partly due to the rejection of the coarse and fine material, which, however, is not actually lost, as it finds its way back in subsequent lots; the actual loss arises from some of the material being carried away in the wash-water, partly in suspension and partly in solution.

COMPOSITION AND PROPERTIES OF SMALTS.—

Smalts is a pigment of a violet-blue shade by daylight which changes to a reddish-blue by gaslight; its colouring power is very weak, and hence it is not much used. The greatest consumers were bleachers, but its use for this purpose has much declined of late years. The tint of smalts varies from time to time, somewhat according to the proportions of the ingredients which have been used in its manufacture, and to the purpose for which it is used; in fineness of powder it also varies a little, and the depth of colour depends largely upon this feature; the finer the powder, the paler the shade or tint of the smalts. It mixes with both oil and water, but in neither case does it make a good pigment for water- or oil-painting.

In composition it is essentially a cobalt glass—a double silicate of potash and cobalt, with a few minor impurities; Rivot gives the following analysis of a sample of smalts:—

Silica, Si O_2 ,	56.4	per cent.
Alumina, $\text{Al}_2 \text{O}_3$,	3.5	„
Ferric oxide, $\text{Fe}_2 \text{O}_3$,	4.1	„
Cobalt oxide, Co O ,	16.0	„
Calcium oxide, Ca O ,	1.6	„
Potash, $\text{K}_2 \text{O}$,	13.2	„
Lead oxide, Pb O ,	4.7	„
		<hr/>	
		99.5	

The composition of smalts varies very much, especially in the amount of the impurities.

It is not acted upon readily by acids or alkalis, which two points differentiate smalts from other blues; by these and its tint it can be readily distinguished. As a pigment it is permanent, perfectly resisting exposure to light, air, &c. It can be mixed with all other pigments without affecting them or being affected by them.

Smalts is sold in a variety of tints and qualities, distinguished by marks, to which some makers attach a meaning, such as FC, fine colour; FCB, fine colour Bohemian; FE, fine eschel; MC, medium colour; OC, ordinary colour, &c. These marks vary with different makers and represent no standard in quality or tint.

ASSAY AND ANALYSIS OF SMALTS.—Smalts requires assaying for its tint or colour, colouring power, and fineness of powder.

As smalts is rarely, if ever, adulterated, an analysis is rarely required, either qualitative or quantitative. The action of dilute acids will soon show whether a sample of smalts has been adulterated with ultramarine or some of the copper blues, while the action of alkalis will soon distinguish the addition of Prussian blue. Smalts is absolutely unaffected by these two reagents.

Long digestion with strong hydrochloric acid decomposes it, leaving a residue of gelatinous silica and forming a solution of the chlorides of the metals it contains.

COBALT BLUE.

This blue is much used by artists on account of the purity of its tint and its permanency.

PREPARATION OF COBALT BLUE.—Cobalt blue is essentially a compound of the oxides of cobalt and alumina; some makers add phosphoric acid in making it; there is some small advantage in doing so, the tint being a little finer.

One method of making cobalt blue is to mix together solutions of alum and cobalt in the proportion of 1 lb. of cobalt nitrate to 12 lbs. of alum; to the solution of these two bodies sufficient carbonate of soda is added to completely precipitate them; the precipitate is collected, placed in a crucible, and heated to a red heat; when the blue colour has properly developed, the mass is washed with water, dried, and ground up for use.

The best method of making it is to dissolve nitrate of cobalt in water, and to add to the solution sufficient sodium phosphate to precipitate all the cobalt as phosphate of cobalt; this precipitate is collected on a filter, and well washed with water. A solution of alum or alumina sulphate is precipitated with one of sodium carbonate, the precipitate is collected and washed with water. The two precipitates are now mixed together in the proportion of 8 parts of the alumina to 1 of the cobalt phosphate precipitate, and the mixture is heated to a bright red heat in a crucible for from half to three-quarters of an hour; when the blue has fully developed, the mass is ground with water and dried, after which it is ready for use.

PROPERTIES AND COMPOSITION OF COBALT BLUE.—Cobalt blue has a greenish-blue tint, which is very fine, although it has a tendency to become of a slightly violet tint under the influence of gaslight. It is quite permanent

when exposed to light and air, and hence is largely used by artists, especially water-colour artists, as it works better in water than in oil. Cobalt blue can be mixed with all other pigments without affecting them in any way, or being altered itself; this is a feature of some considerable importance. It is unaffected by treatment with either acids or alkalies.

It is a compound of the oxides of alumina and cobalt, with, occasionally, some phosphoric acid. The following analysis of a sample, made by the author, will serve to show the average composition of cobalt blue:—

Water,	3·075 per cent.
Alumina, Al_2O_3 ,	80·795 ”
Cobalt oxide, Co O ,	15·132 ”
Alkaline salts,	·998 ”
	<hr/>
	100·000

ASSAY AND ANALYSIS OF COBALT BLUE.—Cobalt blue is rarely subjected to any tests for purity or other properties. Its tint, colouring power, &c., can be examined by the usual methods. Its tint and unalterability by treatment with alkalies and acids serves to distinguish cobalt blue from other blues.

By strongly heating cobalt blue with strong sulphuric acid for some time it is decomposed, a violet solution and a white powder being obtained; on diluting with water, the latter dissolves, and a clear blue solution is obtained, which can be examined by the usual methods of metal analysis.

Cobalt blue has been sold under a variety of names, such as Gahn's ultramarine, Thenard's blue, cobalt ultramarine, azure blue, &c.

COPPER BLUES.

There are a few blue pigments which owe their colour to copper. At one time some of these were very largely used for painting of all kinds, but they have had to give place to ultramarine, which is at once a more powerful colour and more permanent. They are not expensive colours, but are only used now to a very limited extent by artists, and scarcely, if at all, by house-painters. The copper blues are known under a variety of names:—mountain blue, Bremen blue, lime blue, blue verditer, &c. All these blues have a similar composition and very similar properties.

MOUNTAIN BLUE.—This blue pigment (the azurite of

mineralogists) is found naturally, and is essentially a basic carbonate of copper, having the composition:—

Copper oxide, Cu O,	69·2 per cent.
Carbonic acid, C O ₂ ,	25·6 „
Water,	5·2 „
		<hr/>
		100·0

which corresponds to the formula $2 \text{Cu C O}_3 + \text{Cu H}_2 \text{O}_2$.

For use as a pigment the mineral is ground up very fine; it is of a fine tint of blue, and is much more permanent than any of the other copper blues. It is not much used as a pigment.

BREMEN BLUE.—Bremen blue is a pigment of a pale greenish-blue tint without much colouring power; at one time it was made on a large scale, but is now replaced by ultramarine and cobalt blue, so that now it is only made on a limited scale. There are several ways by which it can be made.

1. $125\frac{1}{2}$ lbs. of common salt and 111 lbs. of copper sulphate are ground together into a paste, with water; this results in the formation of chloride of copper and sulphate of soda. With the paste is mixed about 1 cwt. of clean copper, in small pieces about 1 cubic inch in size. All these are thoroughly mixed together and kept in wooden boxes or tubs; at intervals of two or three days the mass is turned over with a wooden spade, so as to ensure that the metal and the paste are brought into intimate contact with one another. In about three months all the copper will have been converted into a green basic oxychloride of copper, which was at one time sent out as a pigment under the name of Brunswick green; this basic oxychloride is insoluble in water, and, after it has been formed, the mass is thrown into tubs and thoroughly washed with water, by which means all the soluble alkaline compounds are washed out. The green is now ready for being converted into the blue; to effect this the green is mixed with a small quantity of hydrochloric acid and allowed to stand for 24 hours; to the pasty mass is then added about $2\frac{1}{2}$ times its volume of caustic soda, at 40°Tw. , which is thoroughly mixed with it; and then the mass is allowed to stand for 36 to 48 hours, by which time it will have been converted into the required blue; it is now thoroughly washed with water to free it from soda, and dried, when it is ready for use.

2. 50 lbs. of sulphate of copper and 26 lbs. of common salt are dissolved with a small quantity of water, heat being used to facilitate the operation. The solution is gradually poured into a solution of 50 lbs. of soda crystals, when a precipitate of copper

carbonate is formed; on allowing this to stand for some time it is gradually changed into basic chloride of copper, and as a considerable effervescence occurs, owing to the liberation of carbonic acid, large vessels must be used. After being washed, the green chloride is transformed into the required blue by the same process as described above.

3. A cheap method of making Bremen blue consists in making a solution of sulphate of copper, to which is added a solution of chloride of calcium or of chloride of barium as long as a white precipitate falls; this is allowed to settle, and the clear blue liquor obtained is mixed with a quantity of freshly-prepared milk of lime until all the copper has been precipitated. This is known by allowing the precipitate to settle and noting the colour of the liquor; if this is blue, then more lime is required. As a rule, 20 lbs. of quicklime is sufficient, when converted into milk of lime, to form 100 lbs. of sulphate of copper. The precipitate is allowed to settle, washed, and dried; while the clear liquor, which is a solution of chloride of calcium, may be used to precipitate fresh sulphate of copper. The results are not so good as with the methods described above.

Bremen blue consists mostly of hydroxide of copper, $\text{Cu H}_2 \text{O}_2$, with small quantities of carbonate of copper.

BLUE VERDITER.—Blue verditer is a pigment of a sky-blue tint. It is very similar to Bremen blue in its composition and mode of preparation.

1. A solution of copper sulphate of 1.312 ($62\frac{1}{2}^\circ$ Tw.) specific gravity is prepared and heated, and a hot solution of calcium chloride added until no further precipitate is obtained. The mixture is filtered, and the liquor, which consists of a solution of copper chloride, is diluted with water until it has a specific gravity of 1.157. Slaked lime is thoroughly ground with water to a great degree of fineness, and added to the copper solution in small quantities at a time, until all the copper has been precipitated. The mixture is now filtered, drained, and washed, and a small portion of the paste weighed and dried as rapidly as possible to ascertain the amount of actual dry colour it contains. The green paste thus obtained is placed in wooden tubs, and for every 35 lbs. of dry colour it contains, 4 lbs. of the lime paste, made as above described, and $2\frac{1}{2}$ pints of a solution of carbonate of potash of 1.116 ($25\frac{1}{4}^\circ$ Tw.) specific gravity is added, and thoroughly stirred with it. The mass is allowed to stand, and, when the proper shade has been developed, it is washed with water, filtered, and dried, when it is ready for use.

2. Another method, which is really an extension of the last

method, is used in some works in Germany. The process is, up to the stage of producing the green paste and mixing it with lime and carbonate of potash, identical with the last method; but, now, the paste is placed in vessels which can be hermetically sealed, and to every 35 lbs. of dry colour there is added a solution of 1 lb. of ammonium chloride, and 2 lbs. of copper sulphate, in $3\frac{1}{2}$ gallons of water; when all are mixed together, as thoroughly as possible, the vessels are closed up, and left for four to five days, after which they are opened, and the colour washed and dried in the usual way.

3. A solution of copper sulphate or nitrate is prepared, and to it is added a solution of either the carbonate of potash or the carbonate of soda as long as a precipitate falls down; this is collected and washed, then treated with a weak solution of caustic soda to turn it blue (as is done in making Bremen blue).

Any copper solution may be used, but the nitrate or chloride gives the best results.

What is called "refiners' blue verditer" is prepared from the copper solution obtained in refining gold or silver. It differs in no way from the verditer prepared from other copper solutions.

A sample of refiners' blue verditer, examined by the author, had the following composition:—

Copper carbonate, CuCO_3 ,	77·797	per cent.
Copper sulphate, CuSO_4 ,	9·426	„
Copper oxide, CuO ,	12·350	„
Water, hygroscopic,	·775	„
	<hr/>	
	100·348	

Another sample of blue verditer had the composition:—

Copper carbonate, CuCO_3 ,	62·45	per cent.
Copper hydroxide, CuH_2O_2 ,	31·19	„
Water, hygroscopic,	3·29	„
Calcium sulphate, CaSO_4 ,	3·07	„
	<hr/>	
	100·00	

Blue verditer is used to a small extent by artists, especially in water-colours; but it is not a permanent pigment.

LIME BLUE.—Before the introduction of artificial ultramarine lime blue was very largely used for fresco-painting, and common lime-washing and distemper work, on account of its resisting the action of alkaline vehicles and pigments. It has, however, gone out of use, so much so that it is extremely difficult to procure a genuine sample of lime blue, ultramarine being sold for it under the name of lime blue.

Lime blue can be made by the following methods:—

1. 125 lbs. of copper sulphate are dissolved in water, and to the solution is added $12\frac{1}{2}$ lbs. of sal-ammoniac dissolved in warm water; 30 lbs. of good clean quicklime are carefully slaked with water, and the slaked lime ground into a fine paste with water, after which it is made into a milk by adding more water. The milk of lime is poured into the copper solution, both being well mixed by constant stirring; when all the lime has been added a blue precipitate and a blue solution will be obtained; this mixture is allowed to stand until the solution has become colourless, taking care to stir it up from time to time while the decoloration is proceeding. The blue pigment formed is filtered, washed with water, and dried.

2. A strong solution of sulphate of copper is prepared, and to this is added sufficient ammonia to redissolve the precipitate first obtained. The solution is heated slightly, and to it is added milk of lime, prepared as in the preceding method; the blue gradually precipitates, and is collected, washed, and dried.

Lime blue is essentially a mixture of copper hydroxide and calcium sulphate.

In preparing all these copper blues care must be taken not to have the liquors too hot, as, if so, there is a liability for the copper precipitate to be decomposed and the black oxide of copper to be formed.

PROPERTIES OF THE COPPER BLUES.—As the properties of the copper blues are so similar a general description will suffice. All the copper blues are characterised by being of a pale greenish-blue tint, varying a little in shade and colouring power; being opaque, they are good pigments, especially in water, but in oil they lose some of their opacity. Although not quite permanent, yet they resist a considerable amount of exposure to light and air; they are blackened by sulphuretted hydrogen or by sulphur, owing to the formation of the black sulphide of copper; on this account they cannot be used in places where they are likely to come in contact with sulphur or sulphur gases, nor can they be mixed with other pigments containing sulphur. Exposed to heat they blacken, owing to the loss of water and of carbonic acid and the formation of the black oxide of copper. Acids dissolve them, forming blue solutions which give the characteristic tests for copper, such as the deep blue solution with ammonia and the brown precipitate with ferrocyanide of potassium. Alkalies have little action in the cold; but when heated with them they turn black, owing to the formation of the black oxide of copper.

Ammonia usually has a solvent action on the copper blues, forming a deep blue solution; by the tests here given copper blues can be readily distinguished from other blues.

The copper blues are rarely met with, their place having been taken by ultramarine and cobalt blue.

CÆRULEUM.

Under the name of Cæruleum two pigments are known; one of these is, or rather was, an old one used by the ancient Egyptians in the decorations of their temples and tombs; this pigment was a very permanent one and of a fine tint of blue, but nothing is now known as to how it was made, although, lately, a French chemist has announced that he has made this colour in all its original properties.

The other pigment is a more modern one, of a fine tint, but of no great permanence. The two pigments will now be described as fully as is necessary.

CÆRULEUM.—The fine blue pigment found on the paintings and decorations of the ancient temples of Pompeii, Alexandria, Cairo, and other old cities testifies how largely it was used by the ancient Egyptians, who were, in all probability, the discoverers of it. So far as can be discerned, the paintings on these ancient temples are of as bright a blue colour now as on the day when they were painted, although they have been exposed to the weather for more than 1,000 years. There is no trace of its manufacture and use after the barbarian invasion of Italy.

The blue has been examined by Chaptal, Sir Humphrey Davy, Girardin, and others, but without any result, so far as its preparation was concerned; and, yet, if it could be produced at a low price it would be very extensively used by all classes of painters.

A more recent observer, Fouque, has examined this pigment, and in a memoir communicated to the Academy of Sciences of Paris, and published in the *Comptes Rendus*, 1887, pp. 108, 325, he describes the results of his analyses of the blue, and of his experiments for its production. Fouque gives the composition of this old pigment as

Silica, Si O ₂ ,	63·7 per cent.
Calcium oxide, Ca O,	14·3 „
Copper oxide, Cu O,	21·3 „
Ferric oxide, Fe ₂ O ₃ ,	0·6 „
	<hr/>
	99·9

He considers it to be a double silicate of copper and calcium, having the formula $4\text{SiO}_2, \text{CaO CuO}$; the iron being, as might be expected from its small amount, an accidental impurity. The ancients, he considers, obtained it by fusing together roasted copper ore with sand and lime.

Fouque states that he has obtained a blue colour of a similar composition in a crystalline condition; the crystals were dichroic, appearing of a deep sky-blue tint when seen by surface reflection, and of a pale rose tint when seen through the edges. There are a few practical difficulties in its preparation, which consist in heating to a bright red heat a mixture of its component parts; if the heat becomes too high, then the blue colour disappears and only a green coloured glass is obtained. The blue pigment thus obtained is said to be quite permanent; it remains unaffected when boiled with sulphuric acid, soda, or lime, or any other alkali or acid; and it is unaffected by sulphuretted hydrogen.

Peligo's Blue is a similar preparation made by fusing together 73 parts of silica, 16 parts of copper oxide, 8 parts of lime, and 3 parts of soda; the temperature must not be allowed to exceed about 800°F ., or the colour will be changed from a blue to a black; if the soda was omitted in this process, the results would be nearer those of the original blue. Peligo's blue has not come into use.

CÆRULEUM (2).—Messrs. Rowney & Co. have offered to artists a fine light blue of a greenish tone, for which they adopt the name *cæruleum*; it is a compound of the oxides of tin and cobalt and is a fairly permanent pigment. The method of producing it has never been published, but, possibly, it is made by preparing a solution of stannate of soda and precipitating this with a solution of cobalt nitrate; the precipitate will consist of a mixture of the oxides of cobalt and tin; the precipitate is heated to a bright red heat, when the blue pigment will result. Another method is to mix together solutions of tin and cobalt, and precipitate with soda; after washing free from the alkali, the precipitate is heated as before. By using silicate of soda as the precipitating agent, so as to obtain a precipitate containing silica, tin, and cobalt, a fine blue could be obtained.

Several other bodies of a blue colour have been suggested for use as pigments, but, partly on account of their greater expense, they have not been able to compete with ultramarine or Prussian blue as pigments; hence, their use has been either limited or abandoned. One may be mentioned.

Manganese Blue.—Some years ago Bong gave a description of the process of making manganese blue, which resembles very

much that of ultramarine. He gives the following mixtures which may be used:—(1) 3 parts of silica, 6 parts of soda ash, 5 parts of calcium carbonate, and 3 parts of manganese oxide. (2) 3 parts of silica, 3 parts of manganese oxide, and 8 parts of barium nitrate. (3) 2 parts of kaolin, 3 parts of manganese oxide, and 8 parts of barium nitrate. In each case the mixture is heated to a red heat in an oxidising atmosphere. Iron must not be present in the ingredients. By varying the proportion of manganese the intensity of the blue can be varied, but not its tint; on the other hand, by increasing the proportion of alkali and silica the blue becomes more violet or green.



CHAPTER VII.

BROWN PIGMENTS.

THIS group of pigments is a small one—umber, vandyke-brown, sepia, manganese brown, Cappagh brown, and one or two others of little importance complete the list. Most of these browns are natural pigments.

UMBER.

Probably the most important of the brown pigments is umber. It is an earthy pigment closely resembling the ochres and siennas in its composition and properties; in fact, these three pigments form a natural group of yellow to brown colours having the ochres at one end of the scale and the umbers at the other, while between the two extremes it is possible to find all or nearly all the intermediate tints or shades.

Umbur is found native in many places; as in Derbyshire, Devonshire, Cornwall, Wales, &c., in this country; in France; in Italy; and in many localities in America. The finest umber comes from Cyprus.

It is found in veins and layers of varying thickness in rocks of all geological ages, and from which it has, in some cases, been derived by decomposition. At Ashburton, near Dartmoor, the umber is found in a layer of from 20 to 30 feet in thickness, overlying the bed rock, which is a dolomitic limestone containing some manganese and iron and from which it has been formed; above the umber there is an overburden of soil.

Umbur varies somewhat in hue from a reddish-brown to a violet-brown, the former hue being characteristic of the Derbyshire umbers, while Turkey umber (which comes from Cyprus) has a warm violet-brown hue. This umber owes its trade name to the fact that it was imported through Constantinople, and its real source was at one time not properly known.

Umbur is sold in three forms—raw lump umber, raw powdered umber, and burnt umber.

Raw lump umber is the pigment just as it is obtained from the

mines. The method of mining will vary somewhat according to the varied conditions under which the umber is found. At Ashburton it is mined by taking off the overburden of soil, digging square pits until the bed rock is reached, and lining the pits with timber as the material is removed. When the bottom is reached these timbers are removed and fresh pits sunk. A similar method is probably in use for mining other deposits of umber.

Powdered raw umber is the lump umber ground and levigated in the same manner as ochres are treated.

Burnt umbers are the raw umbers calcined at a red heat in a furnace, by which treatment the colour becomes darker and warmer; the change which occurs is similar to that which ensues when ochres and siennas are calcined (see pp. 105, 136, 141).

COMPOSITION AND PROPERTIES OF UMBERS.—

Umbers have, as has already been stated, a great resemblance to the ochres and siennas in their composition; but they contain more manganese, which probably accounts for their darker colour. The following analyses of various colours will serve to show the average composition of these pigments:—

	1.	2.	3.	4.
Water, hygroscopic,	4·325	13·475	6·612	65·00
Water, combined,	8·450	5·175	10·250	4·80
Silica, Si O ₂ ,	29·566	4·430	24·518	12·30
Calcium carbonate, Ca C O ₃ ,	5·560	2·607	6·090	...
Manganese, Mn O ₂ ,	12·285	11·530	7·110	10·00
Alumina, Al ₂ O ₃ ,	2·735	8·078	12·802	...
Ferric oxide, Fe ₂ O ₃ ,	36·475	22·500	29·983	6·30
Barium sulphate, Ba S O ₄ ,	30·105
Calcium sulphate, Ca S O ₄ ,	2·153	2·137	...
Phosphoric acid,	trace
Lime, Ca O,	·60
Loss, &c.,	1·00
	99·394	100·053	99·502	100·00

No. 1 is an analysis of Cyprus umber; this sample had a dark, warm brown tint.

No. 2 is an analysis of crude Derbyshire ochre; this sample was of a soft character and of a reddish-brown tint.

No. 3 is an analysis of a sample of umber, probably of English origin. This sample had a yellowish-brown tint. The above analyses were made by the author.

No. 4 is an analysis made by J. J. Beringer (quoted by Frecheville*) of the umber from Ashburton, already referred to; and the next shows the composition of the dolomitic limestone from which it is derived.

Water, hygroscopic,	0·8 per cent.
Calcium carbonate, Ca C O_3 ,	46·7 „
Magnesium carbonate, Mg C O_3 ,	41·0 „
Silica, Si O_2 ,	3·3 „
Ferrous carbonate, Fe C O_3 ,	2·6 „
Manganese carbonate, Mn C O_3 ,	2·5 „
Loss, &c.,	3·1 „
	<hr/>
	100·0

The decomposition has probably been brought about by the dissolving action of carbonated water on the calcium and magnesium carbonates, so as to leave the iron, manganese, and silica behind to form the umber; the amount of limestone which must have been disintegrated to form deposits of umber, 20 to 30 feet in thickness, must have been enormous, as but little of the calcium and magnesium remains behind in the umber. The umber found at Veryan (near Truro), Milton Abbot, and other places in Cornwall is undoubtedly formed from limestone rocks in a similar manner.

Umbers are pigments of a warm brown colour, varying in hue from yellowish to violet-brown. By calcining, the colour is rendered darker and warmer. As pigments, they work well in both oil and water, and they can be mixed with all other pigments without any change occurring. They are perfectly permanent, being unaffected by all the ordinary conditions to which pigments are exposed. Umbers, therefore, meet with extensive use among all classes of painters.

Umbers are not readily attacked by acids, but prolonged digestion with strong hydrochloric acid dissolves the larger proportion of the umber, forming a brownish-yellow solution containing iron, alumina, manganese, and lime; the silica and the barium sulphate remain undissolved. The metals may be tested for by the usual analytical methods. Caustic soda has no action on umbers.

ASSAY AND ANALYSIS OF UMBERS.—Umbers may be assayed for colour or hue, colouring power, covering power, and similar properties by the usual methods.

A chemical analysis of umbers is rarely required, as they are rarely, if ever, adulterated, except possibly a dearer umber by a

* *Trans. Roy. Geolog. Soc., Cornwall*, xvii., p. 217.

cheaper one; but this kind of adulteration would be very difficult to detect. In case an analysis is required the method detailed under oxide reds (p. 108) is applicable here.

VANDYKE-BROWN.

Next to umber the most important brown pigment is Vandyke-brown, so named after the great painter, who was particularly partial to the use of browns in his pictures. No record remains as to the origin of the particular brown which he used, but, it was presumably a natural brown found, perhaps, in the vicinity of the artist's residence and, probably, more or less organic in its origin. The Vandyke-browns now sold are, however, all of artificial production from a variety of sources. In many works on pigments it is stated that this pigment is prepared by calcining ochres and copperas; it is extremely doubtful whether these browns were ever made in this way, as neither ochres nor copperas yield Vandyke-browns when calcined.

Vandyke-browns are made in several ways:—

1. From natural deposits of a brown colour occurring much in the same manner as the ochres and umbers, but differing from them in being derived largely from organic sources, such as peaty matter mixed with more or less earthy matter. Sometimes these pigments are named after the localities in which they are found, as, for instance, Cassel earth.

For use as pigments these natural products simply require to be ground as fine as possible.

2. From cork cuttings and waste, bark and twigs of trees, and other organic matter of vegetable origin, by calcining slightly in a closed vessel.

These Vandyke-browns have a warm brown colour of a reddish hue; they mix very well with oil and water, and can be used for all kinds of painting.

An analysis of such a brown made by the author showed it to have the following composition:—

Organic matter and water,	70·289	per cent.
Calcium carbonate, CaCO_3 ,	3·490	„
Oxide of iron and alumina,	1·615	„
Alkaline carbonates and alkaline salts,	24·606	„

100·000

3. Most of the common Vandyke-browns are made by mixing together lamp-black, vegetable black, or other black pigment with

red oxide and a little yellow ochre; the proportions used vary according to the quality and shade of the oxide used, and whether ochre is also used. Vandyke-browns thus made, and containing from 36 to 50 per cent. of black (chiefly lamp-black) form the great bulk of these pigments as used by the house-painter. This variety of Vandyke-brown is a permanent pigment, and works well in oil, if care be taken in regard to the quality of the black used; if it has any fault, it is that of being a bad drier. In water it does not mix quite so readily as the other varieties of Vandyke-brown, although, when mixed, it works well.

Vandyke-brown is sold in the form of small angular pieces, powder, and paste ground with either oil or water according to the use it is to be put to.

PROPERTIES OF VANDYKE-BROWN. — Vandyke-brown is a perfectly permanent pigment and withstands any amount of exposure to light and air. It works well in either oil or water and with any kind of vehicle. It can be mixed with all other pigments without any alteration whatever.

SEPIA.

Sepia is a brown pigment of slightly varying hue, much used by artists, especially for monochrome work. It is obtained from various species of cephalopodous animals, such as *Sepia officinalis*, *Sepia loligo*, &c. These animals have a peculiar gland which secretes a blackish-brown liquor that collects in what is called the ink-bag. This liquor is secreted for the purpose of defence; when an enemy approaches, some of the contents of the bag is discharged, and this, owing to its strong colouring powers, colours the water for some distance around, and under the cover of the opacity thus produced the sepia makes its escape. The animals are caught and the ink-bag carefully taken out and dried; it then forms the pigment known as sepia. The commercial article is in the form of small pear-shaped pieces of a blackish-brown colour, to which fragments of the sac or skin of the bag usually remain attached. For purposes of use as a pigment for artists it is necessary to remove the sac or bag; this is done by boiling the crude sepia with a solution of soda, which dissolves the colour but not the bag; the liquor is then filtered, and to the filtrate acid is added to precipitate the pigment; the precipitate is collected, washed, and dried.

Sepia is a blackish-brown pigment of very fine texture, mixing well with both oil and water. It is somewhat transparent, but its colouring power is very great, and it is capable of being so

used as a water-colour as to show a great variety of tints and shades; it is this property which makes it of value for monochrome work to artists; no other pigment is capable of being used in this manner with so much facility.

Sepia is a compound of calcium and magnesium carbonates, with an organic colouring principle; Prout has analysed it, and gives its composition as

Melanin or black pigment,	78·00 per cent.
Calcium carbonate, Ca C O_3 ,	10·40 "
Magnesium carbonate, Mg C O_3	7·00 "
Alkaline sulphates and chlorides,	2·16 "
Organic mucus,	0·84 "
	98·40

The black pigment may be isolated by boiling the bag, first in water, which takes out the alkaline salts; then in hydrochloric acid, which takes out the calcium and magnesium carbonates; then, after washing with water, filtering, and drying, the pigment is ready for use.

Sepia is a fairly permanent pigment, being but little affected by exposure to light and air. It is not altered by admixture with any other pigment.

CAPPAGH BROWN.

This pigment is of a reddish-brown hue, and much resembles raw umber both in appearance and composition. It is found at the Cappagh Mines of Lord Audley, which are situated about 10 miles from the town of Skibbereen, in the county of Cork.

Prof. A. H. Church gives * the following analysis of Cappagh brown:—

Water, given off at 100° C.,	18·7 per cent.
Water, given off at a red heat,	11·6 "
Ferric oxide, $\text{Fe}_2 \text{O}_3$,	34·4 "
Manganese dioxide, Mn O_2 ,	27·2 "
Alumina, $\text{Al}_2 \text{O}_3$,	2·6 "
Lime, Ca O ,	1·1 "
Magnesia, Mg O ,	trace.
Silica, Si O_2 ,	4·6 "
Phosphoric acid, $\text{P}_2 \text{O}_5$,	0·4 "

There were traces of organic matter, but not enough to show that it had been derived from bog earth or peaty matter. It is

* Church, *Chemistry of Paints and Painting*, p. 206.

possible that part at least of the manganese, if not the whole of it, existed in the pigment in the form of the red oxide, Mn_3O_4 .

When heated above $100^\circ C$. it acquires a rich red colour not unlike that of burnt sienna.

Cappagh brown works well in oil- or water-colour, and is a permanent pigment. Its qualities as an oil colour are much improved by a preliminary drying at a temperature not exceeding 75° to $80^\circ C$. It has been much used by artists since its introduction.

MANGANESE BROWN.—This brown is an oxide of manganese. It is prepared artificially from the waste still-liquors of the chlorine manufacturer, by precipitating these with sodium carbonate, collecting the precipitate, and calcining in a furnace to a low red heat, until samples taken out and allowed to cool show that the pigment has acquired the desired shade. It is a good and permanent pigment, but it has such excessively-strong drying properties as to make it very unusable as a pigment; hence it has gone out of use. The manufacture of manganese-brown was patented in 1871 by Rowan.

COLOGNE EARTH, CASSEL EARTH, RUBENS BROWN, and other browns are pigments of natural origin of varied composition; some partake of the character of brown lignite of a soft character, others more nearly resemble the umbers in their composition. Their value as pigments is very variable, and, as their composition cannot be depended upon as being constant, it is advisable to avoid the use of these pigments for all artistic painting.

BONE-BROWN is made by gently calcining bones until they acquire a brown colour; it resembles bone-black in composition, but contains some undecomposed animal matter; it is not much used.

PRUSSIAN BROWN.—This pigment is rarely met with now. It was prepared by gently calcining Prussian blue, and hence is a mixture of ferric oxide and carbon; necessarily the pigment was a costly one, and it has no advantage over such pigments as umber or Vandyke-brown.

BISTRE.—This pigment is prepared from the soot of wood, especially from that of beech wood, which gives the finest quality. The soot is collected and washed with hot water until the latter does not extract any more soluble matter from it; sometimes the soot is subjected to a preliminary grinding before the washing. The bistre is dried, and is then ready for use. Bistre is not used as an oil-colour. It has a fine warm brown colour of a yellowish hue. Its permanence depends very much

on the character of the wood-soot from which it is made; sometimes this contains much tarry matter which is not completely extracted from the bistre by the washing operation; the larger the quantity present in the bistre the more fugitive is the pigment. The tarry matter oxidises on exposure to light and air, and the tint becomes, in consequence, paler.

ULMIN BROWNS are pigments made by heating organic matter with alkalies; they are not used, as they are too fugitive.

ASPHALT or **BITUMEN OF JUDEA** was used as a pigment by many of the older artists; but, as time has brought out its many defects, artists have ceased to use it. It enters very largely into the manufacture of varnishes—partly as a colouring matter, partly as a resinous matter. It is described in the section on varnish materials.



CHAPTER VIII.

BLACK PIGMENTS.

NEARLY all the black pigments in use, certainly all those which are most used, are composed either of carbon itself or have that element as their colouring principle. Although carbon exists naturally, yet its native form is not used as a pigment in painting, as it lacks the properties required for that purpose; therefore all the black carbon pigments are made artificially.

Such carbon-blacks are known under a variety of names; lamp-black, vegetable black, carbon-black, are almost, especially the last two, pure carbon; animal-black, bone-black, ivory-black, drop-black, Frankfort black, are blacks prepared from animal and vegetable matters, and contain various other constituents besides carbon.

Besides the pigments just named, and which are specially prepared for use as pigments, carbon is also obtained in other forms, such as coke, charcoal, soot, &c. Some of these are more or less black, and they have been proposed for use as pigments after being subjected to grinding and washing, but they do not make good pigments, and it is doubtful whether they are so used at the present time. Certain natural minerals, such as coal and carbonaceous shale, have also been proposed to be used as pigments, but, as with those just noted, the proposal has probably never been put into practical use.

Carbon is an elementary body belonging to the group of non-metals; its chemical symbol is C, and its atomic weight 12. It is a combustible body in all its forms; in burning it combines with oxygen to form carbon dioxide (carbonic acid gas), $C O_2$, whence it follows that all the black pigments of which carbon forms the principal or only constituent are combustible; a fact which sometimes makes itself apparent in a disagreeable form during the process of manufacture. It is a perfectly stable element, and will remain unaltered by exposure to the atmosphere for any length of time.

Acids and alkalis have no action on carbon. All forms of

carbon-blacks are perfectly permanent pigments, and are unsurpassed in permanency by any other pigment. They can be mixed with all other pigments without bringing about any alteration.

Some of the blacks have slight peculiarities, as will be noticed in the descriptions of them.

LAMP AND VEGETABLE BLACKS.

These two pigments are closely allied as regards the method of their preparation and their composition ; as a matter of fact they are made together at the same time and by the same operation. Lamp-black is probably the most common and most used of the black pigments. Essentially it is a kind of soot. Whenever a combustible body, such as an oil, or fat, or grease, is burnt under such conditions as to preclude complete combustion, then a large volume of smoke is produced, and this deposits a black soot on any surface it may come in contact with ; such soot has a strong black colour and is highly prized as a pigment. Owing to the fact that the earliest convenient means of producing this black was by burning the oil in a lamp under conditions, easily attained, which would ensure that the combustible would not be completely burnt, the black has derived its name of lamp-black. Very little lamp-black is now made by burning oil in a lamp, partly because materials are now used in its preparation which cannot be burnt with good results in a lamp.

The materials used in the manufacture of lamp and vegetable blacks are very varied, and comprise all kinds of oils, fats, coal-tar oils, and greases ; in fact, anything that will yield a great deal of black smoke while burning, preference being given to those which are cheapest and least available for any other purpose. There are some differences in the quality of the blacks yielded by the different kinds of materials used ; the fatty oils and greases yield the best blacks ; the hue is better and the black is finer and less greasy than that from any other kind of grease. The greases from coal-tar give fair blacks ; they are rather browner in hue than the blacks from the fatty oils, and more inclined to be oily from some of the material volatilising at the high temperature at which it is burnt. The residues from the distillation of shale give fair blacks, but are liable to contain traces of volatile unburnt matter. This oily volatile matter in the blacks from coal-tar and shale greases has the effect of causing the black to be a bad drier when used as an oil-paint.

The process of manufacture of lamp-blacks consists essentially in burning the material and collecting the soot. The plant

required consists, then, of two parts—1st, a lamp or furnace in which the material is burnt; 2nd, chambers in which the black collects.

1st Method.—An old method (not much used now, as it is only capable of making lamp-black from liquid oils which are comparatively costly) consisted essentially in burning oil in lamps and collecting the soot. One of the most modern forms of the plant used is shown in Fig. 24, from which it will be seen to consist of a lamp, A, constructed on the bird-fountain principle; the shape of the lamp varies in different places, but the essential features consist of a wick-holder, *a*, constructed to burn a short, wide, or thick wick, to which a liberal amount of oil is supplied

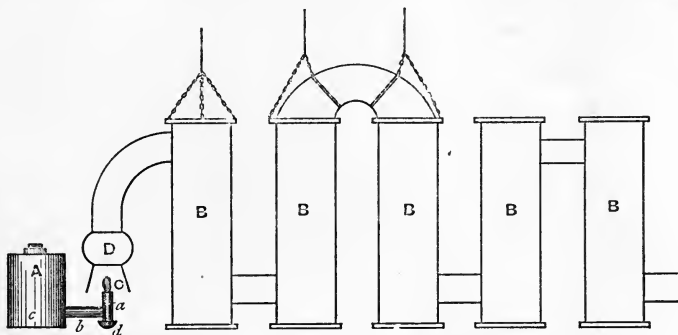


Fig. 24.—Plant for making lamp-black.

by the pipe, *b*, communicating with the bottom of the oil-container, *c*; by thus giving a plentiful supply of oil a very smoky flame results, which is the condition necessary to produce the largest amount of lamp-black. There should be a cup, *d*, at the bottom of the burner to catch any oil which may overflow from the top of the wick-tube. The oil-container, *c*, is so constructed that it is quite air-tight when placed in position, and can only be supplied with air by an air-tube which connects the wick-tube with the oil-container; this air-tube is small, and is so arranged that when the wick-tube is full of oil the opening into the tube is closed, thereby excluding the air, and so stopping the flow of oil from the oil-container, *c*; when, owing to the consumption of oil during the burning, the level of the oil in the wick-tube falls below the opening of the air-tube, then air passes into the oil-container and causes some oil to flow out into the wick-tube through the tube or pipe, *b*. By this means the supply of oil to the wick can be kept very uniform during the process of

manufacture, which uniformity is a necessary condition in the successful making of lamp-black. The collecting chambers consist of a series of strong cylindrical jute or linen bags, B, B, B, B, which alternately communicate with one another at the top and bottom, as shown in the drawing; these bags are suspended by means of chains from a hook in the ceiling of the shed or room in which the operation is carried on. Over the burner of the lamp is placed a large funnel, C; this opens into a large pipe, D; from this proceeds a pipe, *p*, passing into the top of the first bag; the soot from the lamp passes up the funnel and into the large pipe, D; here some of the unburnt oily matter (which nearly always accompanies the soot) collects; then the soot passes on into the bags, the heaviest black collecting in the first bags, while the finer black passes on into the last bags; the heavier portions are sold as lamp-black, while the finer portions are sold as vegetable black. The bottoms of the bags are made to open, so that the black can be shaken from the bags into barrels placed underneath. The bags may be made to communicate with one another by means of large curved tubes; or they may communicate by means of short, straight tubes placed near the top of the bags (see Fig. 24). The collecting bags are about 12 to 15 feet in length and about 3 feet in diameter. The last bag communicates with a chimney, so as to secure the necessary draught and ensure the black being drawn through the bags. It is usual to place a flue between the bag and the chimney; in this flue are placed a number of gauze frames on which collect the last portions of the black. Usually a number of these apparatuses are placed side by side.

The black in the first two bags is kept separate from the black in the other bags, as it is liable to contain unburnt oil, which is a frequent cause of the black entering into spontaneous combustion. To prevent this occurring it is customary to calcine this oily black in a closed furnace, thereby destroying this oil and making the lamp-black better for use as a pigment.

One of the objections to this form of plant is the inflammable character of the material with which it is made; and as it is liable to take fire its use is becoming obsolete, especially as a great deal of waste greases from coal-tar, shale-oils, &c., are used in the preparation of these blacks, which greases are not suitable for burning in lamps.

2nd Method.—The method most commonly used for the production of lamp and vegetable blacks, especially where heavy oils (such as creosote or anthracene oils from coal-tar and the residues of shale-oil distilling) are used, which will not burn

in a lamp, is as follows:—A long brick chamber (of varying size at different works, but averaging about 50 to 60 feet long by 10 feet wide and 7 feet high) is constructed, having the roof flat or slightly inclined to one side. At one end is constructed a furnace similar to a common household boiler, with the fireplace outside the building; the iron pan used is shallow, and, therefore, exposes a great surface in comparison with the quantity of oily material used. A pipe from the exterior of the chamber opens just above the pan, and this is in communication with a reservoir of the oil. The interior of the chamber is divided into a number of compartments by brick partitions, which, however, do not extend quite across the chamber, but stretch alternately first to one side and then to the other of the chambers, thus compelling the smoke from the burning oil to take a circuitous course through the chamber before it passes out at the other end into the chimney of the works.

The distance between each partition is about 4 feet, so that in a chamber 50 feet long there will be about twelve partitions; the more there are of them the better will be the condensation of the lamp-black; still, they must not be too narrow, or the workmen will not be able to get into them to remove the black.

The process of manufacture consists in placing a quantity of oil, &c., in the pan of the boiler, and heating it by means of a fire; when it gets hot enough it ignites when a light is applied, and, owing to the large extent of surface exposed, and, therefore, the limited amount of air in contact with it, it burns with a very smoky flame; as fast as the oil burns away the supply is kept up by allowing oil to drop through the pipe from the reservoir, care being taken not to supply the oil faster than it burns off in the pan, as this might cause the hot oil to overflow, and so produce a fire. The smoke and gases produced by the burning of the oil pass through the chamber, and the black gradually collects in the various compartments; the coarser particles in the first compartments, and on the floor of the others; the finer particles on the roof of the middle compartments, and over the whole of the end compartments. Usually three qualities are collected—heavy, medium, and light; the two former are sold as lamp-black, while the latter is sold as vegetable black. This black weighs about 6 lbs. to a 40-gallon barrel; that from the sides of the flues or compartments weighs about 8 lbs., and the heaviest about 9 lbs.

From time to time the flues and compartments are swept out, the workmen passing from end to end of the compartments for that purpose; the bottom is swept first, then the sides, and

finally the roof. The portion collected in the first compartment is frequently contaminated with unburnt oil, which has become volatilised by the heat of the furnace, and condensed again when it reaches a cold place. This oily lamp-black should always be collected separately, as the oil it contains often causes spontaneous combustion in the lamp-black.

A different method of constructing the chamber is used in some works. In this case the partitions do not run from side to side, but from bottom to top, large openings being left alternately in the top of one partition and the bottom of the next. The chamber is of about the same size as the last described, and has a similar arrangement for burning the oil. This form of plant (shown in Fig. 25) necessitates a door being provided for every compartment, whereas in the last form of plant one or, at the most two, doors only are required. In some cases a large room is provided at the end of the chamber into which the gases, &c., pass before reaching the chimney; here the last particles of black condense, so that gaseous matter only passes into the chimney.

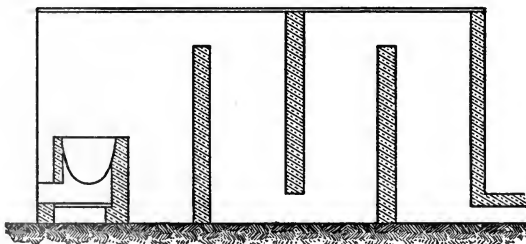


Fig. 25.—Lamp-black chambers.

The amount of lamp-black obtained by any of the processes just described varies very much; it depends upon the kind of oil or grease used, as well as on the completeness of the combustion and of the condensation, the effect of which on the yield must be obvious. Approximately the yield may be taken as 25 to 30 per cent. of the weight of the oil used. The relative proportions of lamp and vegetable blacks produced vary considerably.

3rd Method.—The arrangements described above are those in general use, but are capable of very great improvement. A lamp-black furnace of an improved construction was patented in 1879 by *Messrs. Winslow, Humphrey & Buttrick*. It is shown in Fig. 26. A number of these furnaces are usually arranged

in a row in front of condensing chambers, such as are used in the older methods. From the front wall, *a*, of the condensing chamber projects an iron plate, *f*, which is supported on suitable brickwork; this forms the floor of the fire-chamber, *e*; the pot, *o*, is kept at a red heat, and receives the oil or other suitable

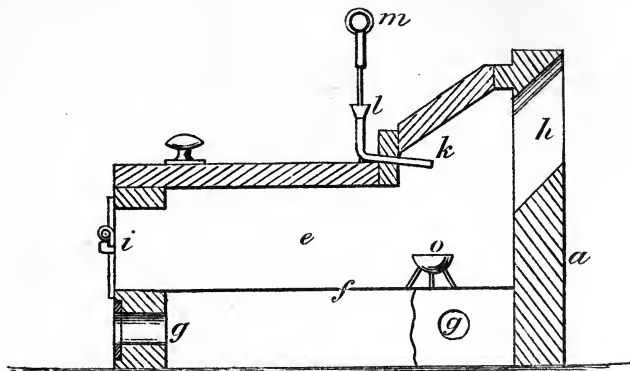


Fig. 26.—Lamp-black furnace.

material in drops from the pipe, *l k*, connected with the main supply pipe, *m*; this oil burns with a more or less smoky flame, and the products pass through the opening, *h*, into the condensing chamber. A quantity of the oil will drop on to the iron plate and enter into combustion; this serves to keep the plate and the pot, *o*, red hot. To prevent the temperature getting too high, a considerable air-space is left under the plate, while the openings, *g g*, admit, and allow the circulation of, air. *i* is a door by means of which the admission of air for the combustion of the oil is regulated. A comparatively low temperature is required and should be just above the burning point of the oil; this, however, varies, some oils burning below 500° F. and others above 600° F.

The whole arrangement being outside the condensing chamber is readily accessible for the purpose of regulating the amount of oil, the temperature of the furnace, and other details affecting the production of the black.

4th Method.—A somewhat different method was patented in 1880 by *Nawrocki*. The oily matters used were burnt in a series of lamps arranged in a row, the oils being heated, if necessary, to ensure proper combustion. Above the burners was arranged an iron plate, against the bottom of which the

flames from the burners impinged; consequently, the combustion was rendered incomplete. This plate is circular in form and made to revolve; it is kept as cool as possible by the upper surface being divided by ribs into a number of compartments through which a constant stream of cold water is made to flow. The action of the apparatus is as follows:—The lamps are lighted and the plate caused to revolve; the black forms on the plate where it is in contact with the oil flames, while the revolution of the plate continually brings a fresh surface for the deposition of the black; as the plate revolves it comes into contact with scrapers, which scrape off the black into suitable receptacles, so that a fresh, clean, and cold surface of the iron plate is always exposed to the flames, and the maximum amount of black is produced by the combustion of the oil.

The process is a slow one, and the yield of oil-black is not so great as in the processes above described. The black obtained in this way is rather more granular in its formation, and has a tendency to be somewhat harder and greyer in tint. Should, by any accident, any of the black be exposed to the action of the flames for too long a period, it is liable to be overburnt, and is thereby rendered hard and almost unusable as a pigment.

5th Method.—In America a large quantity of black is produced by the combustion of the natural gas which flows out of the ground in many of the oil regions. This black is made in large quantities, and sold under the names of gas-black or carbon-black. The principle on which its manufacture is based is the same as that of the last method—viz., the cooling of the flames of the burning gas by iron plates. The form of these plates has altered during the time which has elapsed since the industry was introduced; at first stationary plates, with long trough-shaped upper surfaces, were adopted, and were kept cool by means of a current of water; these were found to be subject to certain defects. Thus, water was condensed on the lower surface, which interfered with the proper condensation of the black, and made the latter damp; then, the black formed, not being immediately removed from the action of the flames, was burnt, and became granular in form, greyer in tint, and much harder. For the purpose of removing the black from the plates, scrapers were passed over the depositing surface from time to time. Of late, these fixed depositing plates have been replaced by revolving plates or cylinders which, during the time the black is being deposited, automatically revolve, and so the black as it is formed is removed from the action of the flames, and, therefore, cannot be overburnt. As the plates or cylinders

revolve, they come into contact with fixed scrapers, which remove the black from the surface as fast as it is formed. Carbon-black differs from oil-lamp blacks in being granular in form, and rather denser; it is blacker in hue than any of the other black pigments. For grinding this black, steel mills are preferable to stone mills. It is the purest form of carbon-black, made quite free from any trace of the unburnt oil often present in lamp-blacks, and from any trace of mineral matter. (See *Oil and Colourman's Journal*, June, 1891.)

PROPERTIES AND COMPOSITION OF LAMP-BLACKS.—Lamp-black is in the form of a black, flocculent powder with a fine texture; in hue it is, usually, what is termed a jet-black, although some samples have a faint brownish tinge. It has great colouring and covering powers. It is rather difficult to mix with various vehicles, especially with water, but, when mixed, it works well as a paint; it dries rather badly when used as an oil paint, especially those samples which contain unburnt oil. It is perfectly permanent as a pigment. It is sold in the form of powder and also as a paste ground with oil, of which it takes 27 per cent.; or with turps, of which it takes 55 per cent. to form a stiff paste.

Vegetable black is a more voluminous black than lamp-black, of a deep jet-black colour and very fine texture. Its colouring and covering powers are rather greater than those of lamp-black. Carbon-black has similar properties to vegetable black, but has a slightly more granular structure.

These blacks are used for making printing inks, varnishes, paint, and for other purposes where a fine black pigment is required.

Lamp-black consists almost entirely of carbon, but there is a small quantity of moisture and mineral matter present in all samples. Vegetable and carbon blacks are nearly pure carbon. The following analyses of lamp and vegetable blacks will show their average composition:—

	Lamp-Blacks.		Vegetable Blacks.	
	1.	2.	1.	2.
Carbon, - -	93·5	94·994	98·87	99·7
Water, - -	4·4	1·806	0·71	0·3
Ash, - - -	2·1	3·200	0·42	...

Samples of lamp-blacks are sometimes met with containing small quantities of oil; these come from the first condensers; such lamp-black is defective, for two reasons—1st, the oil prevents the paint made from the black drying properly; 2nd, the oil is liable to cause spontaneous combustion, so that it is no uncommon occurrence to find a cask of lamp-black almost red hot after standing some time.

ASSAY AND ANALYSIS OF LAMP-BLACKS.—The blacks just dealt with can be assayed for colour, colouring power, and covering power by the usual methods. Lamp-blacks should contain but a small quantity of mineral matter, not exceeding about 3·5 to 4 per cent. To determine the amount, 2 grms. should be weighed into a platinum crucible, and the black heated over a Bunsen burner until all the carbon is burnt off, and nothing but a greyish ash remains; the crucible and its contents are now weighed, and the weight of the ash ascertained. Water can be determined in the usual way. The difference between the amount of water and ash and 100 may be taken as carbon. If the black shows signs of its containing oil, the amount of this impurity may be ascertained by treating a known weight, say about 5 grms., with petroleum ether in a Soxhlett extraction apparatus. The petroleum ether will take out the oil; the ethereal solution is run into a weighed glass, and the ether evaporated off in the water bath; the combined weight of the glass and oil is taken, and the amount of oil ascertained. Vegetable blacks are analysed in the same way; they should have no oil, and should not contain more than 0·5 per cent. of water, or 0·25 per cent. of ash. Carbon-blacks should resemble vegetable blacks in their composition.

BONE-BLACK.

Bone-black, or animal black as it is often called, is prepared from bones by a process of charring them in a closed vessel; the organic matter they contain is decomposed, much volatile matter is given off, and carbon is left behind along with the mineral matter of the bones.

The process of making bone-black may be carried on under two conditions—1st, the volatile products are not collected; 2nd, they are collected. The first plan is the one generally adopted, as there is very little use for the oily matter, known as Dippel's or bone oil, which is obtained by the dry distillation of bones.

1st Process.—When the volatile products from the charring

of the bones are not collected, the black is obtained by breaking up the bones into small fragments and placing these in clay crucibles, fitted with a cover, which is not fastened down; this arrangement allows the volatile matter to escape, but excludes the air, the access of which would cause the carbon to burn away. Any kind of furnace for heating crucibles will answer. One form of such furnace is shown in Fig. 27. The furnace has a flat hearth, measuring $7\frac{1}{2}$ yards long by 5 yards wide, and in the

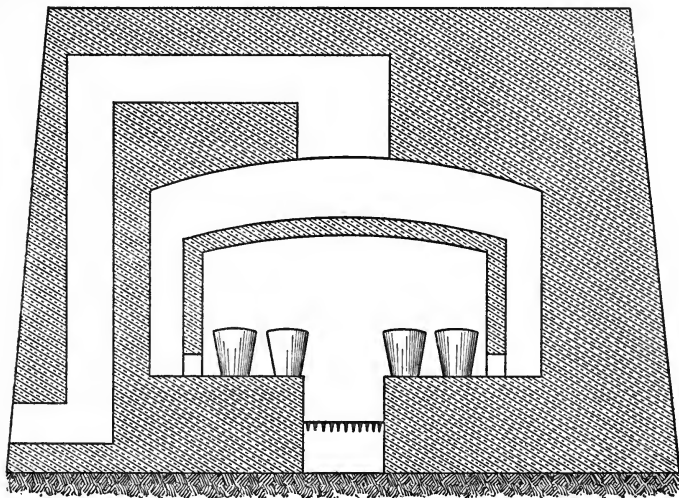


Fig. 27.—Bone-black furnaces.

centre is placed the fireplace, which is fed from the outside. A low firebrick arch extends over the hearth, from the bottom of which a number of flues pass round to the top of the arch, where they are in connection with the single large flue that carries away the products of combustion of the fuel used and the small proportion of volatile matter from the bones which is not burnt up in the furnace. Doors are provided in the sides of the furnace and the arch for the purpose of introducing the crucibles. The crucibles are made of fireclay, and are usually eighteen in number; each is provided with a lid; in some places this is simply placed loose on the crucible, in others it is luted on with clay, a few holes being left for the purpose of permitting the escape of the volatile matter from the bones. When all the crucibles are placed in position in the furnace the doors are bricked up and

the fire lighted. The temperature is slowly raised to a red heat, at which it is maintained for from six to eight hours. The temperature should be kept as uniform as possible during the whole of this period; at the end the fire is withdrawn and the furnace allowed to cool down. Comparatively little fuel is required as the bones give off a good deal of combustible matter, which assists in heating the furnace.

When the furnace is sufficiently cool, the doors are opened and the crucibles withdrawn; it is not usual to allow the furnace to cool down completely, but only sufficiently so as will allow the workmen to enter and work comfortably; to let the furnace get quite cold means a loss of time, and, therefore, fewer charges worked in a given time, as also a greater consumption of fuel to heat up the furnace to the required temperature. It is important, however, that the crucibles should not be opened until they and their contents are quite cold; if opened while they are hot, the black contained in them would take fire and burn away, thus leading to a loss of material. When the furnace is emptied of one charge it is ready for filling with a second charge. Two charges can be easily worked in a day in such a furnace, and, by working hard, three charges may be got through, each charge being about half a ton, and yielding about 60 per cent. of its weight of black.

After the black is taken from the crucibles it is ground in a mill, care being taken to exclude grit and other materials liable to generate sparks by friction and thereby to set fire to the black. If the black is to be used as a pigment, it is ground into a fine powder; if it is to be used for decolorising purposes, it is ground into a coarse granular material.

2nd Process.—When it is desired to collect the volatile bodies given off during the process of charring the bones, the operation is usually carried out in earthenware retorts, such as is used in the distillation of coal or wood; a red heat being used. The volatile portions are passed through a series of condensers formed of iron tubes exposing a large surface to the cooling action of the air, by which operation they are separated into three portions, viz. :—(1) an aqueous liquor containing a fair proportion of ammonia, which can be recovered by the usual methods; (2) oily or fatty matter having a very peculiar and unpleasant odour, which may be used for preparing lamp-black, and is used, to a small extent, for currying leather; and (3) an uncondensable gas, which can either be discharged into the atmosphere or used, if necessary or thought desirable, as fuel for heating the furnaces.

This method of preparing bone-black is rarely used. It is important that after the operation is ended that the fires be withdrawn, and the retorts be allowed to cool down completely before they are emptied; if opened while hot the black will take fire.

PROPERTIES AND COMPOSITION OF BONE-BLACKS.—Bone-black, as sent out for use as a pigment, is a fine powder, of a greyish-black hue, varying a great deal in various samples. It has not the brilliant hue of lamp-black, nor its depth of colour. As a pigment it is quite permanent, and works well in both oil and water, mixing easily with both these vehicles. It is a slow drier when used as an oil-paint. The chief use to which bone-black is put is in the preparation of blacking, where the large quantity of calcium phosphate and carbonate it contains gives to it properties which are as important, perhaps even more important, than its colouring powers.

While bone-black owes its colour to carbon, yet it consists principally of calcium phosphate and carbonate derived from the mineral constituents of the bones. The following analyses, made by the author, of bone-blacks will give some idea of their mineral composition:—

	1.	2.	3.
Water,	24·12	6·19	7·11
Ash or mineral matter,	44·18	77·97	77·75
Carbon,	31·7	15·84	15·14

The first sample contained an abnormal quantity of water for a black pigment, and also contained some lamp-black.

The average quantity of ash contained in bone-blacks is 75 per cent., of which 60 per cent. is phosphate of lime, the rest being carbonate of lime, with traces of silica, iron, and alumina. The carbon ranges from 15 to 20 per cent. As a rule, the ash is white, or of a pale greyish tint; sometimes it has a red tint showing that it contains iron. The author has some suspicion that blacks leaving a reddish ash are not pure bone-blacks.

ASSAY AND ANALYSIS OF BONE-BLACKS.—Bone-blacks can be assayed for tint or colour, colouring power, &c., by the usual methods. An analysis of it may be made in the same way as described under lamp-black. The mineral matter may be further tested if there are suspicions that the sample under analysis has been made by mixing lamp-black with some mineral matter. The ash which is left behind on heating the black in a platinum crucible should almost entirely dissolve in strong hydrochloric acid without much effervescence; on adding ammonia a

copious white precipitate should be obtained; on drying and weighing, this should amount to about 60 per cent. of the weight of the black. To the filtrate from this precipitate ammonium oxalate should be added and the resulting precipitate filtered off, dried, and weighed. The amount of it should be about 15 per cent. of the weight of the black. The precipitate with ammonia should be powdery, not flocculent, in appearance; the latter would indicate the presence of alumina, of which traces only are present in the ash of pure bone-blacks.

IVORY-BLACK.

Ivory-black is, or should be, made from the waste cuttings of ivory by the same process as bone-black is made from bones. Much bone-black is sold as ivory-black. In composition and properties ivory-black resembles bone-blacks. The following are some analyses, made by the author, of ivory-blacks, but the genuineness of the samples is not guaranteed:—

	1.	2.	3.
Water,	7·05	7·41	8·27
Mineral matter,	75·58	76·21	74·86
Carbon,	17·37	16·38	16·87

Ivory-black has usually a finer and more brilliant hue than bone-black. It is used for making printing ink, blacking, &c.

ANIMAL BLACK.

Under the names of animal black and animal charcoal a number of black pigments, made from animal matters of all kinds and by various processes, are sold for use as pigments and for decolorising purposes. Animal black is made, much in the same manner as bone-black, from all kinds of animal products, waste pieces of leather, skins, hoofs, horns, hair, &c. In the process of making yellow prussiate of potash there is produced a large quantity of black, which was at one time thrown away, but it is now largely used for decolorising sugar, paraffin wax, &c.

The composition of animal black is very variable; the following are analyses of several samples of these blacks sent to the author for analysis:—

	1.	2.	3.	4.	5.	6.	7.
Water,	28·75	28·11	36·70	45·50	24·12	27·75	6·19
Ash,	29·22	30·71	34·80	24·70	44·18	0·74	77·97
Carbon,	42·03	41·18	28·50	29·80	31·70	71·51	15·84

No. 6 had a most peculiar fetid odour and contained a quantity of unburnt oil ; from its appearance and composition it is evident that its only claim to the name of animal black was that it was made by the lamp-black process from bone oil.

No. 7 was a true bone-black. With these two exceptions the above analyses show that this black is made from a variety of materials.

Animal black can be used for all purposes to which black pigments are applied.

FRANKFORT OR DROP-BLACK.

This black is named "Frankfort black," because it was first prepared in the old German town ; "drop-black," on account of the shape into which it is made up for sale.

Drop-black is made from a great variety of materials of an organic character, such as vine twigs, refuse of wine-making, peach stones, hop bine, bone shavings, ivory cuttings, &c. These are calcined in a closed vessel until they are thoroughly charred. The black so obtained is then ground up as fine as possible with a little water ; then the mass is lixiviated to free it from soluble matters, and dried. Then it is mixed with a little glue water and made up into pear-shaped drops for sale, for which purpose they are ready when dry.

Drop-black is a black of fine texture, varying in hue from a bluish-black to a somewhat reddish-black, which is due to the different materials of which it is made ; vegetable matters yield a black of a bluish hue, while animal matters give a black of a greyish hue.

Drop-black owes its colour to carbon, the amount of which varies in different samples ; it also contains some mineral matter which will vary in amount and kind according to the character of the material from which the black was prepared. The following is an analysis by the author of a sample of drop-black:—

Water,	2.333	per cent.
Carbon,	65.742	„
Mineral matter,	31.925	„

The mineral matter contained phosphate of lime, which showed that bones had been used in making this sample.

Drop-black is used for all purposes for which black pigments are required.

German black is a synonym for drop-black.

MISCELLANEOUS BLACKS.

Besides the black pigments described above, several other substances may be briefly noticed, which have been proposed for use as pigments, or have been so used on a small scale.

CANDLE BLACK is a kind of lamp-black made on a small and extremely limited scale from the flame of a candle by holding a cold plate over it.

PRUSSIAN BLACK is made by calcining Prussian blue in a closed vessel until the residue has a black colour; this black is a mixture of carbon and oxide of iron, and usually has a brownish tinge; it possesses no advantage over lamp-black and is more expensive.

BLACK LAKE.—When a solution of sulphate of copper and bichromate of potash is added to a decoction of logwood a black precipitate falls down; this, after being washed and dried, forms black lake. Too much bichromate of potash should be avoided, as it has a tendency to turn the lake grey; the substitution of a little sulphate of iron for some of the bichromate improves the lake, while reducing the risk of adding too much of the chrome salt. Black lake is a pigment of a fine hue and texture; it is not permanent when used as a pigment, fading on exposure to light and air.

TANNIN-BLACKS are similar pigments to the last, and are made by adding solutions of either the sulphate or the so-called “nitrate of iron” to solutions of tannin materials, such as sumach, divi-divi, myrobolans, &c. Their production from waste leather has been made the subject of a patent; the leather scraps are boiled in an alkaline solution, which dissolves out the tannin matter used in tanning the leather; to this solution a mixture of alum and sulphate of iron is added and the black precipitated. The tannin-blacks have a bluish hue; they have no great colouring power, and are not permanent when exposed to light and air. They have been very little used as pigments.

CHARCOAL-BLACKS.—These are made by grinding the charcoal obtained by charring soft woods. The grinding should be well done, and the black pigments should be washed with water to remove any soluble matters it may contain. These blacks are mostly sold as lamp-blacks, carbon-blacks, &c. In their general properties they resemble the lamp-blacks, but are a little more granular in texture.

COAL-BLACKS have been made by grinding coal and shale, but it is doubtful whether any are now used.

LEAD-BLACK is the sulphide of lead made, according to the

patent specification, by taking lead-fume (*i e.*, the powder which collects in the flues of lead furnaces) and boiling it for some time with a solution of sodium sulphide. The black soon forms. It is doubtful whether this black has been used on a practical scale. Its permanency is doubtful, as it is possible that it may be prone to oxidation to lead sulphate and, therefore, to decolorisation.

PRUSSIATE BLACK is the black residue (consisting mostly of carbon) which is obtained as a bye-product in the manufacture of yellow prussiate of potash. This is collected and well washed with water, when it is ready for use. It is largely used as a decolorising agent.

MANGANESE-BLACK is the oxide of the metal manganese found naturally and simply ground up very fine for use as a pigment. The great objection to its use as a pigment is its great drying properties. It is also expensive, and possesses no material advantage as a pigment over lamp-black.

Blacks have been proposed to be made from other materials by mixing ochres with peat and similar carbonaceous materials, and calcining the mass in closed vessels. Spanish black is a name given to a black made from cork shavings. The use of the black sulphide of iron was patented by *Claus* in 1882, but it has never come into practical use. Aniline-black has been proposed to be used as a pigment, but its great expense is against its practical use for this purpose. It is made by dissolving aniline hydrochlorate in water, and adding to it a solution of potassium bichromate acidified with sulphuric acid. The black precipitate, which rapidly forms, is collected and washed.

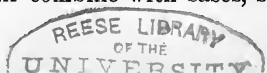
CHAPTER IX.

LAKES.

LAKES form a class of pigments of considerable use in painting. They were among the pigments used by the early Italian painters, from whom their use has descended to the present time. Pliny gives some account of them, and from this description the origin of the name "lake" can be gathered. The early Italian dyers for certain colours used what was known as "lac," which was either the product now known under this name, or an analogous body. This lac requires the aid of tin and alumina compounds before the colour can be developed and fixed on the fabric which has to be dyed; during the process of dyeing some of the colouring matter of the lac combines with some of the tin and alumina to form an insoluble body, which forms a kind of coloured scum on the top of the dye-vat; this substance, known to the Italian dyers as "lacca," was collected, dried, and sold to artists. In the same way other laccæ were obtained when other natural dyestuffs were used; gradually methods of preparing these laccæ were discovered, by which they could be obtained direct from the dyestuffs themselves, without the necessity of troubling the dyer, and thus has arisen the preparation of the lakes, which name can be readily traced to the laccæ of the Italian dyers.

Lakes may be defined to be compounds of an organic colouring principle with a metallic body. The organic colouring principle may be obtained (as it was in the early times, and until very recent years) from natural colouring matters, such as lac, cochineal, Persian berries, fustic, Brazil wood, sapan wood, &c.; or it may be derived from the coal-tar colours, a source which has only lately come into prominence for lake-making, but which promises in the future to supplant the natural colouring matters for this purpose, as they very nearly have done for dyeing textile fabrics.

The colouring principle of most natural colouring matters is of an acid or phenolic character, and will combine with bases, such



as tin, alumina, iron, lead, antimony, &c., to form coloured bodies which are insoluble in water ; as a rule, the affinity between the two bodies is so great that the lake is precipitated when a solution of a metallic salt is added to one of the colouring matter. Theoretically, a lake should be a compound of the colouring principle and the metallic base combined in equivalent proportions ; but, practically, such a lake does not exist ; usually, the base largely predominates. This excess is sometimes accidental, but often purposely made, the object being to modify the shade of the lake, as is the case with Dutch pink, rose pink, and one or two others. Then, again, in some lakes there may be small traces of the colouring principle carried down mechanically with the lake during the process of making.

Lakes are usually made by preparing a decoction of the colouring matter, and then adding to this a solution of the base ; as a rule, the lake forms almost at once ; at other times, the addition of a small quantity of a solution of carbonate of soda is sufficient to throw down the lake. By preparing alkaline solutions of the colouring matter the lake is thrown down at once on adding the solution of base ; this method is not always applicable, as the alkali sometimes affects the shade of the resulting lake, as in making alizarine-lakes.

The colouring matters, or rather their colouring principles, may be divided into two groups. One contains coloured matter, and includes such substances as fustic, Persian berries, and cochineal, which may be called substantive colours, as the colour does not depend upon the mordant or base used ; thus Persian berries will give a yellow lake with either alumina, tin or lead, although there are some minor differences in the tint or shade of the yellow so produced. The other group may be called adjective colours. It comprises substances like alizarine, fresh logwood, &c., in which the colour is only developed when the colouring principle is combined with a base, and differs with the base used ; thus alizarine, when combined with alumina gives a red, while with iron it gives a deep dull violet ; again, logwood with antimony gives a violet, with iron a blue-black, and with chrome a deep blue.

All lakes should be quite insoluble in any vehicle, such as water, oil, turpentine, or spirit, used to make them into a paint ; on the other hand, a true lake is always more or less transparent when used as a pigment, and lakes are, therefore, mostly used as covering or glazing colours to modify the tint of an under coat of paint, and to obtain effects which are not obtainable with opaque pigments. Some lakes are rendered nearly opaque by

mixing the materials during the process of manufacture with some opaque white pigment, by which the body or covering power of the lake is increased, and at the same time the shade is more or less affected. If a lake dissolves in the vehicle, then all its properties as a pigment in regard to its body or covering powers are lost, and a coloured varnish only is obtained which will not do the work it is intended that the lake-paint should do.

In the following pages the lakes prepared from the natural colouring matters will first be described, then those prepared from the coal-tar colours.

RED LAKES.—These can be prepared from cochineal, madder, Brazil wood, barwood, and one or two other natural products; but those named are what are chiefly used commercially. Cochineal yields carmine, crimson, scarlet, Florentine, and a few other lakes. Brazil wood gives rose-pink and some of the cheap red lakes. Madder yields the madder lakes so much prized by artists, but which are too expensive for common house-painting. The other red colouring matters are, owing to special difficulties, not much used in lake-making. It is not intended to give a special description of colouring matters used in the preparation of lakes; if the reader requires such, he should refer to some work on dyeing, such as that by Knecht, Rawson & Löwenthal.

CARMINE.—The best example of a lake is probably the pigment carmine, which is an almost pure lake, a combination of the colouring principle of cochineal (carminic acid) with alumina and tin. The exact method by which it is made from cochineal has never been published, and is probably only known to the few makers of this lake, although various descriptions of processes have appeared from time to time; some of these are very misleading, and have probably been intentionally made so. The pigment has been known for more than 200 years; its discoverer is unknown, although according to one statement it was a Franciscan monk. In 1656 a writer named Homberg published a recipe for making it.

The chemical nature of carmine is even now but imperfectly understood, although it and its source cochineal have frequently been examined. In the main, the various writers agree that carmine is a combination of the colouring principle of cochineal (carminic acid) with alumina; but there is always present small quantities of other bodies, which renders any investigation into its composition a matter of some difficulty.

Liebermann gave, in the *Berichte der Deutsche Chemisch*

Gesellschaft, vol. xviii., p. 1,969, the following analysis of a cochineal-carmine:—

Moisture,	17 per cent.
Nitrogenous matter,	20 ”
Ash,	7 ”
Colouring matter,	56 ”
Wax,	traces.

The ash contained—

Stannic oxide, Sn O ₂ ,	0·67 per cent.
Alumina, Al ₂ O ₃ ,	43·09 ”
Calcium oxide, Ca O,	44·85 ”
Magnesia, Mg O,	1·02 ”
Sodium oxide, Na ₂ O,	3·23 ”
Potassium oxide, K ₂ O,	3·56 ”
Phosphoric acid, P ₂ O ₅ ,	3·20 ”
	99·62

More recently, in the *Journal für Praktische Chemie*, 1890, No. 3, Lafar published the following analysis of carmine:—

	As sold.	Dried.
Water,	15·50 per cent.	... per cent.
Ash,	6·87 ”	8·14 ”
Nitrogenous matter,	23·26 ”	27·60 ”
Colouring matter,	54·37 ”	64·26 ”

The ash contained—

Copper oxide, Cu O,	0·35 per cent.
Stannic oxide, Sn O ₂ ,	0·14 ”
Alumina, Al ₂ O ₃ ,	40·48 ”
Ferric oxide, Fe ₂ O ₃ ,	traces.
Calcium oxide, Ca O,	44·20 ”
Magnesia, Mg O,	0·61 ”
Sodium oxide, Na ₂ O,	5·40 ”
Potassium oxide, K ₂ O,	3·20 ”
Phosphoric acid, P ₂ O ₅ ,	2·71 ”
Silica, Si O ₂ ,	0·60 ”
Carbonic acid, C O ₂ ,	2·31 ”

The two analyses agree with one another as well as analyses of a commercial and variable product like carmine can be expected to agree. The lime and alumina in the ash are in the proportion of 2 Ca O : Al₂ O₃; this circumstance would point to the fact that carmine is not purely an alumina lake, but a lime-alumina lake, with some proteid matter. The tin and copper in the ash have probably been derived from the vessels in which the cochineal has been boiled, as it is often recommended in recipes for carmine-making, to make the decoction

of cochineal in two vessels; the other constituents are of no importance.

The following methods have been published for preparing carmine:—

1. 1 lb. of cochineal is extracted by boiling in water for from 15 to 20 minutes, the decoction is strained off, 1 oz. of alum is added, and the boiling continued for a few minutes longer; the clear liquor is decanted off and 1 oz. of cream of tartar added; the mass is then allowed to stand for the carmine to settle.

2. Boil up 2 lbs. of cochineal, strain off the decoction, add 2 ozs. of alum, 3 ozs. of muriate of tin (a solution of stannous chloride), 2 ozs. of carbonate of soda, and allow to stand for 2 days, when the carmine will have been thrown down.

3. 1 lb. of cochineal is boiled with water and $\frac{1}{2}$ oz. of carbonate of soda; to the decoction is added 1 oz. of alum and 3 drams of cream of tartar; the mixture is allowed to stand for the carmine to be deposited.

4. The following process was patented by *Wood*, in 1856:— 9 ozs. of sodium carbonate, 8 ozs. of citric acid, and 27 quarts of water, are boiled together; then $1\frac{1}{2}$ lbs. of cochineal are added and the mixture boiled for $1\frac{1}{2}$ hours, strained, and clarified; the liquor is heated to the boil and 9 ozs. of alum are added; the mass is then boiled for 5 minutes longer and allowed to stand for 3 days, when the carmine precipitated is collected, washed, and dried.

A recipe was published by *Madame Cenette*, of Amsterdam, a noted maker of carmine, but this is defective, and carmine cannot be made by following it.

In the preparation of carmine it is advisable to use tin or tinned-copper vessels for boiling the cochineal in, as a small quantity of the metal dissolves in the liquor and exerts a beneficial influence on the carmine which is produced. Earthenware vessels may be used, but iron must be avoided, as any trace of iron in solution affects the shade of the carmine rather injuriously. The use of too much alum should be avoided, as it tends to reduce the colouring power of the carmine and also to alter the tint, turning it more crimson, while the shade ought to be a scarlet.

Carmine is a deep fiery-scarlet powder, slightly varying in tint; the best quality is known commercially as “nacarat carmine.” It is insoluble in water, alcohol, ether, turpentine, and all the vehicles used in mixing paints, but soluble in strong mineral acids. In caustic soda, caustic potash, and ammonia solutions, it dissolves with a deep crimson colour, from which

solutions the carmine can be precipitated by exposure to the air or by the addition of weak acids like acetic or tartaric acid; the carmine so obtained is very little changed from the original, so far as tint is concerned. Solutions of salts of iron, lead, &c., have an injurious effect on the tint of the carmine. Carmine, on being heated in a crucible, burns and leaves behind from 7 to 10 per cent. of a white ash, which consists principally of alumina and lime, as will be seen on examination of the analyses given above.

As a pigment carmine works well in either water or oil, and is used, to a small extent, by artists as a glazing or tinting colour. It is not permanent, as a few months' exposure to sun and air is sufficient to impair the brilliancy of its hue, and prolonged exposure causes it to fade.

Carmine is frequently adulterated with other lakes and red pigments. The fact of adulteration may be ascertained by treating the lake with ammonia, when, if pure, it will completely dissolve; if not pure, the adulterant is left as an insoluble residue.

CARMINE LAKE.—In preparing carmine the whole of the colouring matter of the cochineal is not precipitated, and therefore the liquors from the carmine are strongly coloured, and are utilized for the preparation of carmine lake. The usual method of making is to add to the liquors a small quantity of alum (about one-fourth of the weight of the cochineal used in making the liquor originally), a little tin chloride, and then sufficient potash carbonate solution to precipitate the whole of the alum and tin; the precipitate is collected, washed, and dried.

Another method is to make a decoction of cochineal, and to add to this freshly-precipitated alumina (obtained by adding ammonia to a solution of alum, and collecting the precipitate of alumina); the colouring matter is absorbed by the alumina, and a lake is formed; only sufficient of the alumina is added as will produce a lake of the required depth of colour.

1 lb. of cochineal is boiled in water, and 1 lb. of cream of tartar or carbonate of potash is added; then 1 oz. of tin chloride is added, and sufficient alum to throw down all the potash salt and the colouring matter of the cochineal; the lake obtained is collected, washed, and dried.

FLORENTINE LAKE is carmine lake which is, after making, mixed with a small quantity of gum water and moulded into the form of tears or drops. Sometimes cheap qualities of Florentine lake are prepared by mixing the genuine article and a lake made from Brazil wood together.

Crimson-Lake and Scarlet-Lake are prepared from cochineal

in the same way as carmine-lake, but the proportions of alum and tin used differ, and the precipitated lake is moulded into the form of drops.

BRAZIL-WOOD LAKES.—2 lbs. of Brazil wood are digested in 8 gallons of water for 24 hours; then the mass is boiled for half-an-hour or so, strained, and allowed to stand for a few days or a week; this is necessary if the full strength of the wood is to be utilised; the colouring principle in fresh Brazil wood exists in the form of brazilin, which of itself has little colour; but by oxidation it is converted into brazilein, which possesses strong colouring power; this change occurs when decoctions of the wood are allowed to stand for some time. When the decoction is ready there is added to it $1\frac{1}{2}$ lbs. of alum, $\frac{1}{2}$ lb. of tin chloride solution, and then sufficient carbonate of soda to precipitate. The precipitate is collected, washed, and dried.

Another method is to prepare a decoction as before, and to add to this sufficient freshly-precipitated alumina and oxide of tin.

A variety of Brazil-wood lake, which is known as *Vienna lake*, is prepared by mixing 60 lbs. of starch, 20 lbs. of chalk, and 2 lbs. of gypsum with a decoction of Brazil wood; then 2 lbs. of ground alum are added, and the mixture stirred, and allowed to stand for 12 hours; the liquor, which will be fairly free from colour, is decanted off, fresh alum and decoction of Brazil wood added, and the stirring, standing, &c., repeated; this operation is continued until the lake has acquired the desired shade. At first the tone is inclined to be violet-red, owing to the alkalinity due to the chalk; but as this becomes neutralised by the successive additions of alum, the tint becomes crimson.

ROSE PINK is a crude kind of lake of a dull rose-red colour prepared from Brazil wood by making a decoction of the wood in the usual manner, adding some gypsum and chalk, and then precipitating with alumina.

RED LAKE.—In a patent taken out in 1856, *Gatty* describes a process for making a red lake from Brazil wood by adding to 20 gallons of a decoction (sp. gr. 7° Tw.), 1 gallon of antimony chloride at 52° Tw.; filtering, washing, and drying the precipitate.

Messrs. Roberts & Dale patented in 1857 a process of preparing a red lake from barwood. 7 cwts. of barwood are boiled in 500 to 600 gallons of water, and 50 lbs. persulphate of tin diluted with water added thereto; the whole is boiled for 3 to 4 hours, allowed to settle, and decanted; the lake formed is washed, filtered, and dried.

Barwood is not adapted for preparing lakes, as the colouring principle it contains is not soluble in water, and the tin required to produce the lake must be added to the wood directly; as a consequence, the lake so prepared is apt to be contaminated with particles of the wood.

Another method described in the same patent is to boil barwood in a solution of 1 to 1½ oz. of carbonate of soda per gallon of water, whereby the colouring principle is extracted; to the decoction (after straining off the wood) is added sufficient tin chloride to precipitate the lake.

YELLOW LAKES.—Dutch Pink, English Pink, and Italian Pink, are inappropriate names given to lakes of rather a crude kind prepared from quercitron bark. They can be prepared by boiling 2 lbs. of quercitron bark, straining the decoction, and adding 1 lb. of alum; to the mixture is added 4 lbs. of fine Paris white in small quantities at a time; then the mass is placed on one side for 2 or 3 hours, collected, washed, and dried. By decreasing the quantity of Paris white, the shade of the yellow is made deeper. Lakes from quercitron are used in painting theatrical scenery, as they do not lose much of their tint under the influence of gas light.

Another method is to use ½ lb. of fustic extract, and 2 lbs. of gypsum, and to precipitate with ¾ lb. of lead acetate.

YELLOW LAKE.—This is prepared from Persian berries by (a) boiling 1 lb. of the berries with 1 oz. of cream of tartar in 1 gallon of water, straining, and to the clear decoction adding sufficient alum to precipitate the lake. (b) 1 lb. of the berries is boiled with 1 lb. of alum in water; the liquor is strained, and then sufficient carbonate of potash is added to precipitate the lake; care is taken to avoid an excess of the alkali, as this would redissolve the colouring matter. (c) A cheap yellow lake, much employed in painting scenery, is made by boiling 2½ lbs. of Persian berries with 2½ lbs. of turmeric in water for some time, then, after straining the decoction, adding to it 1¼ lbs. of sulphate of alumina and 6 lbs. Paris white, allowing the mass to stand for some time, filtering, washing, and drying.

(d) **Gatty's Process.**—To 20 gallons of a decoction of quercitron (7° to 8° Tw.) is added 1 gallon of antimony chloride at 52° Tw. The lake is precipitated, washed, and dried.

ORANGE-CARMINE or **ORANGE-LAKE.**—1 lb. of Persian berries are boiled in 1 gallon of water and the liquor strained; then ¼ lb. of muriate of tin (commercial stannous chloride solution) added and sufficient sodium carbonate to precipitate the lake, which is collected, washed, and dried. This

lake has a bright orange colour, and is chiefly used by calico-printers.

Orange-Lake.— $\frac{1}{2}$ lb. of fustic extract is dissolved in water, and $\frac{3}{4}$ lb. of lead acetate added thereto.

Orange-Lake.—Precipitate a mixture of fustic extract and annatto dissolved in a little carbonate of soda with alum and tin crystals.

MADDER-LAKES.—These are largely used by artists on account of the brilliancy of their tint and superior permanency over other lakes. Several methods have been published for their preparation.

(a) **Englefield's Process**.—Tie 2 oz. of madder in a piece of thin cloth, and beat it well in 1 pint of water in a stone mortar, and repeat the process with 5 successive pints of fresh water, until the material ceases to yield colour; the mixed liquors are boiled in an earthen vessel, and 1 oz. of alum is dissolved in the pint of water, then a solution of $\frac{1}{2}$ oz. of potassium carbonate is slowly added, and the mixture allowed to stand until cold; the top liquor is decanted off, and the lake well washed in hot water, filtered, and dried.

(b) Macerate 2 lbs. of ground madder in 1 gallon of water for 10 to 15 minutes, and repeat the process with 2 or 3 successive quantities of water; the liquors are mixed and $\frac{1}{2}$ lb. of alum is added; the mixture is gently heated nearly to the boiling point for 3 or 4 hours, filtered, and a solution of sodium carbonate added as long as a precipitate falls; this is filtered, well washed with water, and dried.

(c) 2 lbs. of madder are steeped in tepid water for 26 hours, and a slight fermentation set up, whereby the decomposition of the glucoside of the madder is effected, which means an increase in the colouring power of the extract; to the mass is now added a solution of 2 lbs. of alum, the mixture being maintained at about 150° F. from 3 to 6 hours, when the liquor is strained and precipitated with sodium carbonate as long as a precipitate falls down; the precipitate is filtered, washed, and dried as usual.

(d) Add to the decoction of madder a small quantity of acetate of lead solution, which throws down a brown colouring matter which is present in the dyestuff; after filtering this off, the clear liquor is treated with alum and tin as usual.

(e) Garancine is a more or less purified madder, the useless glucoside (or ruberythric acid) of which has been converted into useful colouring matter, and may be used in the preparation of madder lakes. The process is to treat 1 lb. of the garancine with successive portions of a boiling solution of $\frac{1}{2}$ lb. of alum

in 2 gallons of water, using altogether about 2 gallons; after extraction, the liquor is filtered, and allowed to cool, when the colouring matter separates out as a flocculent precipitate; this is collected and dissolved in ammonia, and to the solution is added alum, or a mixture of alum and tin chloride, sufficient to precipitate the colouring matter. The depth of colour of the lake depends upon the amount of alum used, provided there be sufficient ammonia to precipitate all the alum added; the more alum the paler the tint of the lake.

(*f*) **Persoz Process.**—1 lb. of garancine, and 1 lb. of sodium sulphate are boiled together in 18 pints of water; to the mixture is added 1 lb. of alum, previously dissolved in water, and the mass allowed to stand for some time for the alum to extract the colouring principle of the garancine; the mass is next strained, and to the clear liquor is added 1 lb. of lead acetate; lead sulphate is precipitated, and this is filtered off; on boiling the clear filtrate the lake formed is collected, washed, and dried.

MADDER RED LAKES.—(*a*) By combining both madder and cochineal bright carmine-red lakes can be prepared. A decoction of madder and alum is prepared in the manner described above under madder lakes (*c*); to this is added an ammoniacal solution of cochineal (prepared by digesting 1 lb. of cochineal in 4 ozs. of ammonia diluted with its own volume of water for a few days) as long as a precipitate falls down. This is collected, washed, and dried.

(*b*) A cheap red lake can be made by mixing decoctions of madder and Brazil wood, adding carbonate of soda, and precipitating with alum, or alum and tin, in the usual way. The recipes for preparing madder and Brazil wood lakes may be combined to produce the compound lake.

Madder only contains the colouring principle, alizarine, in comparatively small proportion; with it is associated other colouring matters and impurities, which, as a rule, are more soluble in boiling than in cold water; hence it is necessary to avoid extracting madder with boiling water, otherwise these impurities pass into the extract and injuriously affect the tint of the resulting lake. The bulk of the colouring matter exists in the madder in the form of a glucoside named ruberythric acid; this, by fermentation, is converted into the colouring principle, alizarine. It is well to take advantage of this in the process of preparing madder lake by steeping the madder in a little tepid water for a day or so, and then extracting the colouring principle with alum as described under method (*c*) above.

Madder lakes, when pure, are fairly bright in tint, and good as

regards both their covering and colouring powers. They are almost entirely soluble in solutions of caustic potash or caustic soda, but not in weak ammonia, which character serves as a distinguishing point from carmine. Boiled with dilute sulphuric or hydrochloric acid madder lakes are decomposed, alizarine, the colouring principle of the madder, being liberated as a brownish-yellow precipitate. When used as pigments they are more permanent than other lakes; in dry air they are nearly permanent, but in moist air they fade a little.

GREEN LAKES.—Chinese green and sap green are similar to lakes in composition and properties; they have already been described. There are no other green pigments prepared from vegetable dyestuffs by precipitation as lakes; most of what are sold as green lakes are either lakes made from coal-tar colours (as described below) or with mixtures of either Prussian blue or indigo and gamboge, not true lakes.

VIOLET LAKE.—(1) A violet lake can be made by adding $2\frac{1}{2}$ gallons of antimony chloride, at 52° Tw., to each 16 gallons of a decoction of logwood (10° Tw.). The lake is immediately precipitated, and is filtered, washed, and dried.

(2) 3 lbs. of alum are dissolved in 1 gallon of water, and to the solution is added $2\frac{1}{2}$ lbs. of lead acetate previously dissolved in a little water; the precipitated sulphate of lead is filtered off and the clear liquor is used in preparing the lake. 6 lbs. of logwood are made into a decoction with 10 gallons of water, and to 10 gallons of this liquor 1 gallon of lead-alum liquor is added; the lake precipitated is collected, washed, and dried. It has a fine violet colour, but is not fast.

The lake colours are often sold in the form of pastes for the purpose of colouring beverages, sweets, &c. The author has had occasion to make analyses from time to time of such pigments, and the following are selections from such analyses:—

ANALYSES OF LAKE COLOURS.

	1.	2.	3.	4.	5.	6.	7.
Water, . . .	80·40	80·00	79·45	68·2	79·45	82·0	88·75
Ash, . . .	6·75	9·55	10·20	19·9	10·60	9·3	3·00
Colouring matter,	12·85	10·45	10·35	11·9	9·95	8·7	8·25
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	100·00	100·00	100·00	100·0	100·00	100·0	100·00

1. Scarlet from Lima wood with alumina.
2. Orange-scarlet from peach wood with alumina.
3. A brownish-yellow from Persian berries with alumina.
4. Olive-yellow from Persian berries with lead and chalk.
5. Orange made from fustic and annatto with alum and tin.
6. Violet-brown from Lima wood with alum, lead, and iron.
7. Blue-black from logwood and iron.

General Considerations on Lake-making.—The preparation of lakes is a matter of some difficulty, especially when it is desired to prepare successive batches, perhaps at some considerable interval of time, of the same depth and brilliance of colour. This difficulty arises almost entirely from the variable character of the dyestuffs or colouring matter used, the natural colouring matters varying considerably in actual colouring power; this makes it impossible for the users, either lake-makers or dyers, to always work from very definite recipes; these must be modified from time to time, according to the actual strength of the batch which is being used. If the colouring power of the dyestuff is weak, then more must be used to produce a lake of a given shade than if the colouring power is either normal or above the average; or, if no more dyestuff is used, then the proportion of base must be varied to suit the strength or colouring power of the dyestuff.

The depth of tint or colour of the lake which is prepared depends, as may naturally be inferred, on the proportions of the base or precipitating agent to the colouring matter; the greater the proportion of base the paler will be the tint of the lake produced. As the preparation of lakes is a chemical operation depending upon the combination of the colouring principle of the dyestuff with the base (alumina, tin, &c.), there will be a definite relationship between the two bodies, resulting in the formation of a lake having the maximum depth of colour. What these proportions are has not yet been determined; they necessarily vary with different colouring matters, and even with different batches of the same colouring matters. Any excess of dyestuff used over these proportions does not lead to any increase in the depth of the lake formed, but such excess is left unused, and may probably be thrown away; on the other hand, any excess of base reduces the tint of the lake, as has been explained above.

After precipitation, the lake should be well washed, and dried slowly at as low a temperature as possible. Usually lakes are made up in the form of conical masses, drops, or *troches*; this is done by mixing a small quantity of gum or glue water with the wet lake, then pressing the mass into moulds, or moulding between the fingers, then drying in the usual way.

The following description of the reactions given by various chemical reagents with decoctions of the principal natural dyestuffs used in lake-making may be found of use, especially in the examination of lakes for the purpose of ascertaining how they are made; but it may be pointed out that it will always be advisable for the analyst to make such experiments on his own

account, for the purpose of observing the exact shade of colorations produced, as it is impossible to convey, with sufficient exactitude, an idea of the actual tint of any coloration or precipitate which may be produced.

Cochineal.—Alumina sulphate gives a bright crimson solution; on the addition of sodium or potassium carbonate a crimson precipitate falls down. Stannous chloride gives a dull purplish coloured precipitate; copper sulphate a purple precipitate; ferric chloride a brown precipitate; caustic soda a bluish crimson solution. Strong sulphuric acid changes the colour of the decoction to an amber colour, and, on adding water, a pale yellow solution is obtained.

Brazil Wood.—Alumina sulphate gives a red precipitate. Stannous chloride throws down a pale crimson precipitate; lead acetate a violet-rose precipitate; ferric chloride a chocolate-brown precipitate; copper sulphate a brick-red precipitate; and caustic soda forms a crimson solution. Strong sulphuric acid changes the colour of the decoction to a red-brown, and on diluting this with water a pale amber solution is obtained.

Persian Berry.—Alumina sulphate has no action. On further adding ammonia or caustic soda, a brownish-olive precipitate falls down, while alkaline carbonates throw down a brighter yellow precipitate. Stannous chloride throws down an olive-yellow precipitate, lead acetate a yellow-brown precipitate, and ferric chloride a dark olive-green precipitate. Nitric acid forms a red solution. Strong sulphuric acid forms a yellow-brown solution, and on adding water a brown precipitate falls down.

Quercitron.—Alumina sulphate throws down an ochre-yellow precipitate, stannous chloride an orange-yellow precipitate, lead acetate a dark yellow-brown precipitate, copper sulphate a brownish-olive precipitate, and ferric chloride a dark olive-green precipitate. Caustic soda forms a dark yellow-brown solution, from which acids throw down a yellow-brown precipitate. Strong sulphuric acid forms a brownish-yellow solution, from which, on adding water, a dark brown precipitate falls down.

Fustic.—Alumina sulphate, stannous chloride and lead acetate throw down orange-yellow precipitates; the first is bright, the last rather duller than those with the other two salts. Copper sulphate throws down a dull yellow precipitate, and ferric chloride a dark olive-brown precipitate. Strong sulphuric acid forms a brown-yellow solution, from which, on diluting with water, a brown precipitate falls down.

Annatto.—Alumina sulphate throws down a brownish precipitate, stannous chloride an orange-red precipitate, ferric chloride a red-brown precipitate, while strong sulphuric acid forms a dirty yellow-brown solution.

Turmeric.—Alumina sulphate gives a yellow precipitate, ferric chloride a brownish-yellow precipitate, and stannous chloride a yellow precipitate. Caustic soda forms an amber solution, and strong sulphuric acid a pale yellow solution.

Logwood.—Alumina sulphate changes the colour of the decoction to a crimson-red; ferric chloride throws down a bluish-black precipitate; potassium bichromate causes the formation of a black gelatinous mass after standing a short time; copper sulphate throws down a violet-black precipitate, and antimony chloride a violet precipitate; caustic soda changes the colour of the decoction to a violet, while hydrochloric acid turns it red.

ANILINE-LAKES.

Of late years the use of the coal-tar colours for the preparation of lake-pigments has grown very extensively, and now such lake-pigments are largely used, especially for paper-staining, manufacture of paper-hangings, printing, lithography, &c. In many cases they have displaced some of the older colours, especially such as emerald-green, which are rather poisonous, and vermilion, which is expensive.

The aniline or coal-tar lakes are not true lakes, although they are prepared by precipitating a coal-tar colour with a suitable precipitating agent; they always contain another substance in addition to the lake proper, which is added for the double purpose of increasing the covering power or body of the lake as well as, in many cases, of modifying or toning down the shade; at the same time it reduces the cost of the lake and brings it within the purchasing power of painters for use in common decorative work. Three things are required in the preparation of coal-tar colour lake-pigments—1st, the colour; 2nd, the precipitating agent; 3rd, the base or, as it is sometimes called, the carrier.

1st. **THE COLOURING MATTER.**—The dyestuffs prepared from coal-tar products may be divided into 16 groups according to their chemical composition and relations; but for the present purpose they may be divided into three groups differing from one another in the character of the methods used in preparing lakes from them. Although something like 300 different coal-tar colours are to be found in the market, yet,

for various reasons which will be pointed out later on, many of these cannot be used in the preparation of lake-pigments.

1. **Basic Colours.**—These dyestuffs are salts of certain complex organic bases prepared, in the first instance, from aniline, toluidine, &c. They include such dyestuffs as magenta, brilliant green, auramine, aniline-blue, methyl-violet, Bismarck brown, benzoflavine, rhodamine, &c. These colouring matters form, with certain weak organic acids, such as tannic acid, picric acid, &c., coloured precipitates, and it is on this property that their use in the preparation of lake-pigments is based.

(a) *Colouring matters precipitated by tannic acid.*—All the basic coal-tar dyestuffs are precipitated by tannic acid, but the following are of special value as lake-pigment makers:—magenta, safranine, auramine, aniline-blue, brilliant green, methyl-green, new green, Nile blue, rhodamine, phosphine, methyl-violet, Paris violet, Hofmann violet, Bismarck brown, chrysoidine, quinoline-yellow, benzoflavine, pyronine G. The combination between the tannic acid and the colouring matter is a chemical one and takes place in definite proportions; but, as these dyestuffs are rarely sold pure, only approximate quantities can be given in any recipes for their transformation into lake-pigments. There is one point to be noticed in connection with the precipitation of these basic colours with tannic acid, which is that the precipitated lake has the property of carrying down with it some of the colouring matter in a free form.

It is best to use tartar emetic along with the tannic acid in making the lakes, so as to form a double combination of the tannic acid with the colouring matter on the one hand and with the antimony of the tartar emetic on the other, which has a material influence on the complete precipitation of the dyestuff and on its fastness to light and air.

One fault of the tannic lakes is that when used as oil colours they do not dry well or completely; the cause of this lies with the tannic acid, which exerts a retarding action on the drying of linseed oil, and, if present in large proportions, will almost completely prevent the oil from drying. Hence tannic acid lakes cannot be used with satisfactory results as oil colours, but for all other vehicles they are quite satisfactory. The precipitation of the lakes is more complete if sodium acetate be added; this acts by neutralising the hydrochloric acid which is liberated from the colour by the action of the tannic acid and which exerts a solvent action on the colour lake, the free acetic acid formed from the sodium acetate having no such action. The tartar emetic has a similar action (see below).

(b) *Colouring matters precipitated by picric acid.*—This sub-group includes auramine, night-blue, methyl-blue, methyl-green, brilliant green, safranine, and a few others. Picric acid being itself a yellow dyestuff, it is obvious that the shade of the resulting colour lake must be modified thereby; thus, the greens which are naturally of a blue shade and are so precipitated by tannic acid, are thrown down by picric acid of a yellow-green tone, while the reds take a yellower tone, and the blues become greenish. The picric acid lakes may be used as water-colours, but they cannot well be used as oil-colours, for the oil does not dry properly; they thus resemble the tannic acid lakes, but, if anything, the defect is stronger.

2. **Acid Colouring Matters.**—The term “acid” as here used has special reference to the fact that the colours comprised in this group are dyed on to wool or silk from baths containing a small quantity of free acid and not to the fact that the colours themselves are of an acid character, although many of them are.

Some of them are derived from the basic colours by a process of sulphonation, by which means they are rendered capable of dyeing wool or silk from acid baths, which, previously, they were not capable of doing. The great majority of the acid colours are what are called azo-colours, that is, bodies characterised by containing a group of two nitrogen atoms, $-N=N-$, combined with some organic radicle of a basic or phenolic character; in some colouring matters there is more than one such group. Other dyestuffs belonging to this group are nitro-derivatives, usually of phenols.

These colouring matters are precipitated from their solutions by acids and metallic salts (such as lead acetate, barium chloride, alumina sulphate, alum, zinc sulphate, magnesium sulphate, &c.)

Naturally, they vary much in the degree or ease with which they are precipitated. Some are thrown down by all the agents above noted; others, again, are only precipitated by one or two of the salts. Others, again, require the solutions to be slightly alkaline before they are precipitated. The following lists, showing how these acid dyes are precipitated, will illustrate this point.

(a) *Colours precipitated by lead acetate.*—Lead acetate will precipitate a very large number of the coal-tar colours belonging to the acid group; in some cases the precipitated lake is of sufficient good colour to be of service in making lake pigments, in other cases it is not so. To enter into full details with regard to all the colours would take up more room than can well be spared in this book, but the following list and the notes appended thereto

will be found of use:—Scarlet BB (lake of a poor shade, not serviceable), mandarin G, orange G, orange IV (the lake is of a brownish shade, and not useful), fast scarlet 3R (very good lake), acid mauve B, yellow N (fine shade of colour), croceine-orange, fast red T, alkaline blue, citronine A, tropæoline OO (lake of a very pale colour, not useful), citronine O, methyl-yellow, new yellow, scarlet G, scarlet R, ponceau 2G, fast violet (the lake is but of a poor shade), orchil brown B, fast red A, azo-yellow, double brilliant scarlet 2R, croceine 3B, quinoline-yellow, crystal scarlet 6R, phosphine, scarlet OO, scarlet GT, vermilline scarlet KK, Bordeaux S (very good shade of colour lake), all the eosine colours, benzoazurine R, benzoazurine 3G (gives rather a poor shade of lake), diamine-blue B, Titan pink (gives a dark crimson colour lake), Congo 4R,* chrysamine (gives rather a dark brownish yellow lake), and chrysophenine (a fine precipitate).

(b) *Colours precipitated by barium chloride.*—Scarlet BB, ponceau, orange G (gives a fine bright colour-lake, very useful), orange IV, fast scarlet 3R (a fine bright colour-lake), acid mauve B, claret-red B, yellow N, croceine-orange, croceine-scarlet, fast red T, alkali-blue, Victoria blue B, citronine O, methyl-yellow, new yellow, scarlet G, ponceau 2R, scarlet R, resorcin-yellow, fast violet, orchil-brown B, fast red A, azo-yellow, double brilliant scarlet 2R, Indian yellow, crocein 3B, quinoline-yellow, crystal scarlet 6R (not so good a lake as with lead acetate), naphthol-yellow S, phosphine, scarlet 2R, scarlet GT, vermilline-scarlet KK, scarlet 2RJ (gives a very fine lake), scarlet 3R, benzoazurine R, benzoazurine G, benzoazurine 3G, diamine-blue B, Congo 4R, chrysophenine (gives a good lake), chrysamine (precipitates as a brownish lake).

(c) *Colours precipitated by alumina sulphate.*—Scarlet BB (the lake has a brownish tone), mandarin G, Orange IV, fast scarlet 3R, croceine-orange, alkali-blue, Victoria blue B, citronine O, scarlet G, fast violet (but a poor shade of colour-lake), orchil-brown B, fast red A (but a poor shade of lake), azo-yellow, Indian yellow, scarlet GT, benzoazurine R, benzoazurine G (a good precipitate), benzoazurine 3G, Titan pink, Congo 4R, chry-

* The red colouring matters, which, like Congo-red and benzopurpurine, are derived from benzidine, tolidine and stilbene, are precipitated by lead acetate and other precipitants, but, in consequence of their being sensitive to acids in a great degree, the resulting colour-lake is liable to be much affected in colour by acid precipitants. Thus, Congo-red will give a blue lake instead of a red, and the others are more or less similarly affected; therefore they are practically useless for making lake-pigments.

sophenine (the precipitate has an olive-brown shade), chrysamine (gives a brown precipitate), and diamine-blue B (a fine shade). Sulphate of alumina does not precipitate so many colouring matters as lead acetate or barium chloride, probably on account of its great acidity, which keeps the colour-lakes in solution to a large extent; by neutralising this acidity with soda or ammonia some colours can be precipitated, but the addition of alkali has to be made with great care, or the shade of the colour-lake may be affected. Freshly-precipitated and washed hydroxide of alumina, $\text{Al}_2\text{H}_6\text{O}_6$, has a strong affinity for many of the coal-tar colours of all classes, and this may (as will be shown presently) be taken advantage of in the preparation of lake-pigments.

The remarks appended to group *a* regarding the so-called Congo colours, are applicable to the precipitates obtained with barium chloride and alumina sulphate.

These lists do not pretend to be exhaustive, but they include all the colouring matters which are most useful for this particular purpose. It is well to point out that the same name is given by different makers to different dyestuffs, so that it is quite possible for, say, the scarlet G of one maker to give a precipitate with alumina sulphate, while the scarlet G of another maker will not give a precipitate.

Of the three precipitating agents, barium chloride gives the best and most satisfactory results; although both lead acetate and alumina sulphate give useful colour-lakes; but barium chloride is a more universal precipitant than either of the others, and the colour-lakes it gives are not affected by admixture with sulphur pigments, as is the case with lead acetate colour-lakes, which are apt to go brownish if mixed with pigments containing sulphur or if exposed to the action of sulphur gases.

Lake-pigments made with either barium chloride, lead acetate, or alumina sulphate, are very satisfactory in use, and are serviceable either as oil- or water-colours.

3. Adjective Colouring Matters.—This class of colouring matters was named by Bancroft adjective dyestuffs; their peculiarity is that they are usually not coloured of themselves, and, used alone, are not capable of imparting any colour to textile fibres, but that they require the aid of a second substance, which, in dyeing, is called the mordant, to develop the colour and to fix it on the fibre; further than that the colour which is so fixed on the fibre is largely influenced by the character of the mordant, and with different mordants different colours are produced; thus alizarine, with alumina gives a bright red, with iron a violet, with tin

a scarlet, and so on. The dyestuffs belonging to this group are capable of yielding lake-pigments, which are characterised by their permanence. They are rather difficult to prepare in anything like brilliant hues.

For fuller information relating to the coal-tar colours, the student may consult Benedikt and Knecht's "Chemistry of the Coal-tar Colours," or the author's "Dictionary of the Coal-tar Colours."

2nd. THE PRECIPITATING AGENT.—The nature of the precipitating agents used in preparing lake-pigments has been partly considered while dealing with the coal-tar colours themselves, and very little more needs to be said. Tannic acid is the precipitant for the basic colours. This should be bought of good quality; in fact, for this particular purpose the purer it is the better; the common qualities of tannic acid are more or less adulterated with dextrine, &c., and are slightly coloured, which qualities have an injurious influence on the brilliancy of the pigment thrown down by it. In addition to tannic acid, tartar emetic is used; this adds considerably to the permanence of the pigment, probably for two reasons; one is that the antimony of the tartar emetic combines with the tannic acid to form an insoluble tannate of antimony, and with this the colouring matter combines, thus forming a more insoluble and therefore more permanent pigment; then, again, most of the colouring matters are sold in the form of hydrochlorides of the colour-base, and in the process of making the lake the hydrochloric acid is set free, and may tend to prevent proper precipitation of the lake. When tartar emetic is used the hydrochloric acid acts upon this and combines with the alkali, liberating tartaric acid, which has no action on the colour-lake formed. The addition of sodium acetate has been proposed for the purpose of preventing this formation of free hydrochloric acid.

As regards the precipitating agents used with the acid dyestuffs, viz., barium chloride, lead acetate, alumina sulphate, &c., these should be of good quality, and contain neither insoluble matter nor free acid; this last remark applies more particularly to alumina sulphate, which is apt to contain free acid, whereby the formation of the colour-lake is prevented; in using this agent the addition of sodium acetate to neutralise any free sulphuric acid which may be present, or which may be formed in the process of precipitation, is to be recommended.

For the adjective dyestuffs the acetates of alumina, chrome, &c., will be found to give good results. Many processes for the preparation of pigments from these colouring matters are based

on the formation of the hydroxides by precipitation with sodium carbonate or sodium hydroxide, and then combining this with the colouring matter. This is not a satisfactory method, because the alkali has a tendency to affect the shade.

3rd. THE BASE.—The base or carrier exerts a most important influence on the value of the lake as a pigment; the body or covering power almost entirely depends upon the base, while this also modifies the tint or shade of the pigment very greatly. The base used is commonly one or other of the white pigments (which have already been described), but in one or two lake-pigments other bases, such as red- or orange-lead, is present.

The following bases are used in making lake-pigments:—barytes, whiting, china clay, gypsum, French chalk, zinc-white. For details as to the composition, &c., of these reference is made to the chapter on white pigments.

Barytes is the base most commonly used; the common qualities are apt to be gritty, a fault which must be avoided; further, in making what are called pulp-colours for paper-stainers, barytes is not very useful, as its absorbent properties for water are not sufficiently strong; these colours are required to contain about 50 per cent. of water, while barytes will not take up more than 25 per cent. The artificial barytes, *blanc fixe*, is a good base, and the method of preparing the pigment may be so devised as to cause the formation of this form of barytes during the process of making the lake, and then a pigment of great brilliancy of hue and covering power is obtained; but this method of working is more costly than using the natural barytes.

Gypsum forms a very good base for lakes. It is lighter than barytes; hence it does not make the pigment feel so heavy, and has less tendency to separate by subsidence when made into a paint; it takes up rather more water than barytes, and is therefore better for pulp-colours. In covering power it is about equal to barytes. Precipitated calcium sulphate may now be obtained as a bye-product in the manufacture of many chemical products; this form would be found useful as a base, and better, in fact, than the natural gypsum. Gypsum, weight for weight, takes rather more colouring matter to produce a given shade of lake than does barytes.

China clay makes a good base for these lake-pigments, being quite inert in all its properties, as well as of good covering power and colour. It is largely employed in making pulp-colours, owing to its great absorbent properties for water, in which respect it is superior to either barytes or gypsum; on the other hand, unless a large proportion of dyestuff is used the

resulting lake is apt to appear chalky, on which account china clay is not suitable for making pale-tinted lakes.

French chalk would make a good base, so far as its chemical properties are concerned; but it does not work well as a paint, being apt to be slimy.

Whiting is a fairly good base for lakes, and is largely used for this purpose; although, owing to its somewhat alkaline properties, it does not suit all colouring matters. Like china clay, it is liable to make the lake appear chalky in tone, and, therefore, can only be used in making dark tints. It does not suit lakes made from basic colours, owing to the action of tannic acid on it.

Zinc-white makes a good lake, but its cost is against its meeting with an extensive use for this purpose.

To produce a given shade of lake, barytes takes less colouring matter than any of the other bases noted, and, consequently, a barytes-lake costs a trifle less than does a lake with other bases; next to barytes comes gypsum, which takes from one-and-a-half to twice as much dyestuff in proportion to barytes, while china clay takes rather more than twice as much. Pulp-colours, such as are used by paper-stainers, are made so as to contain about 50 per cent. of water, and, in making these, barytes cannot well be used, as it will only take up about 25 per cent.; the best base for such is a mixture of barytes, china clay, and gypsum, in about equal proportions.

In any case the base should be of a good white colour, and free from any trace of grit. Before using, it should be ground with water, and then sieved, so as to obtain it of as fine a consistence as possible.

PROCESS OF MANUFACTURE.—The method of making pigments from the coal-tar colours is comparatively simple, and does not necessitate the use of any special plant; the only requisites are tanks for dissolving the various colouring matters and precipitating agents, and a tank (like those shown in Fig. 18, p. 118) for precipitating the lake in.

The colouring matter is dissolved in a vat or tub, by simply mixing the dyestuff with water. In the case of those colouring matters which, like some brands of violets and magenta, are sold more or less impure, and in a cake form, it is best to dissolve them in boiling water. A good proportion is 1 lb. of colouring matter to 10 gallons of water. It is advisable to strain the solution before using it, so as to free it from particles of undissolved dyestuff and grit.

The precipitating agent is dissolved in a separate vat and the solution filtered to free it from the dirt and other insoluble matter which would deteriorate the lake.

Into a third vat is placed a quantity of water, which is heated to from 120° to 150° F., and then the base (barytes, china clay, or whatever is used) is thoroughly mixed or diffused through the water, special care being taken to break down all lumps, because these would give the lake a speckled appearance, a thing which is to be avoided. Next, the solution of the colouring matter is run in, thoroughly mixed with the base, and, after heating the whole to the temperatures given, the precipitating agent (in solution) is run in slowly with thorough agitation; when all has been run in, the lake formed is allowed to settle, and the top liquor run off; this should be colourless, or nearly so; if it be strongly coloured, the precipitation of colouring matter has not been complete and more precipitant is added. The lake is now washed by adding clean water and then finished, as may be required, by the usual methods. When required for pulp-colours the lake simply requires filtering off; if required to be dried then, after filtering, it must be dried in the stove at a temperature below that by which the colour or tint of the lake would be affected.

The process here given is generally applicable to all the coal-tar colours, but, in some cases, modification of the details are required, which will be pointed out when dealing with the pigments themselves.

LAKES FROM BASIC COAL-TAR COLOURS.—

Magenta lake.—100 lbs. of barytes, 1 lb. of magenta, 1½ lbs. of tartar emetic, and 1½ lbs. of tannic acid make a lake of a deep crimson colour.

Bluish-pink lake.—100 lbs. of barytes, 3 lbs. of rhodamine. 3 lbs. of tartar emetic, and 3 lbs. of tannic acid. This makes a lake of a peculiar shade of bluish-pink, which is fairly resistant to exposure to light and air.

Pale crimson lake.—100 lbs. of barytes, 2 lbs. of safranin prima, 2 lbs. of tartar emetic, and 3 lbs. of tannic acid. The lake obtained is a fine shade of crimson.

Violet lake.—100 lbs. of barytes, 1 lb. of aniline-violet, 1 lb. of tartar emetic, and 1½ lbs. of tannic acid. The shade of this lake will depend entirely upon the shade of the violet used, which may vary from a violet-red (violet 3 R) to a pure violet (violet 5 B). Either methyl-violet, or Hofmann's violet, or Paris violet may be used.

Blue-green lake.—100 lbs. of barytes, 1 lb. of brilliant green, 1 lb. of tartar emetic, and 1½ lbs. of tannic acid. This gives a very deep bluish-green lake.

Yellow-green lake.—100 lbs. of barytes, 1 lb. of brilliant-green, ½ lb. of auramine, 1½ lbs. of tartar emetic, and 2½ lbs. of

tannic acid. This gives a very nice yellow-green lake; by varying the proportions of the two dyestuffs a great variety of green lakes can be made and also a very good imitation of emerald-green may be obtained by their means.

Yellow lake.—100 lbs. of barytes, 3 lbs. of auramine, 3 lbs. of tartar emetic, and 4 lbs. of tannic acid. This lake is very good and a tolerably permanent one.

Orange lake.—100 lbs. of barytes, 2 lbs. of chrysoidine, 4 lbs. of tannic acid, and 2 lbs. of tartar emetic.

Brown lake.—100 lbs. of barytes, 2 lbs. of Bismarck brown, 2 lbs. of tartar emetic, and 4 lbs. of tannic acid.

In making all these lakes the barytes is mixed with water and the tartar emetic is placed in the same tub or vat, the colouring matter added, and the tannic acid (previously dissolved in another tub) run in slowly; after which, the lake is finished as described above. In the place of barytes any other of the above-mentioned bases can be used. By using mixtures of the dyestuffs in various proportions, as, for instance, safranine and auramine, brilliant green and Bismarck brown, a great variety of lakes of various colours can be prepared.

Another method of preparing lakes from basic coal-tar colours is to use picric acid, as in the following case:—

Yellow-green lake.—100 lbs. of barytes, 1 lb. of brilliant green, and 1 lb. of picric acid. The barytes and green are diffused through water as usual and, when ready, the picric acid (previously dissolved in water) is run in; the lake precipitated is finished as usual.

Another process of making lakes from basic coal-tar colours consists in precipitating them with resinates of alumina or magnesia. This is carried out as follows:—100 lbs. of rosin are dissolved by boiling in a solution of 10 lbs. of 77 per cent. caustic soda, and of 33 lbs. of soda crystals in 100 gallons of water; when the rosin has completely dissolved, 5 to 15 lbs. of the dyestuff are added, the quality used being varied according to the depth of colour of lake required. Then a solution of magnesium or alumina sulphates are added in slight excess; the lake precipitated is collected, washed, and dried. These resinate lakes are soluble in alcohol, benzene, chloroform, ether, &c., and are, therefore, used for colouring varnishes.

LAKES FROM ACID COAL-TAR COLOURS.—The number of acid coal-tar colours, especially the reds, is very great, and it is impossible in this work to enumerate and mention what lakes can be made from these dyestuffs; the examples given will, however, serve to illustrate the principles on which the conver-

sion of acid coal-tar colours into pigments are based, and enable any intelligent colour-maker to apply them in producing a lake from any colouring matter belonging to this group.

Among the lakes of this group are the vermilionettes and royal reds.

VERMILIONETTES AND ROYAL REDS.—Vermilionettes were introduced to this country some twelve or fourteen years ago by the Silicate Paint Company of Liverpool, as a substitute for vermilion, which they have displaced to a considerable extent. Royal reds were introduced by Messrs. J. B. Freeman & Company of London. These pigments, and some others, sold under a variety of fancy names (such as Victoria reds, signal-reds, &c.) owe their brilliant colour to eosine; the deeper shades of the vermilionettes and the royal reds also contain orange lead; this is used for two reasons, one is to make the pigment heavy, and a closer imitation of vermilion, the other is to increase the depth of colour and the body.

These two pigments are made in a great variety of tints, from a very pale pinkish-red to a very deep scarlet; most makers keep several shades of both in stock. Vermilionettes are now made from barytes and eosine, with a precipitating agent, although, when first introduced, they contained orange lead as well, and some makes do so now; royal reds contain both barytes and orange lead as well as the eosine. The precipitating agent most used is lead acetate, although alum is also used occasionally.

The tint and brilliancy of these pigments depend largely upon the kind of eosine used. There are several varieties of eosines made, of which the following are the principal. They are all very bright scarlet dyestuffs, and may be divided into blue-shade eosines and yellow-shade eosines, distinguished by the marks B or BN for the former, and by J or G for the latter; these being the most useful for vermilionette-making:—

Eosine A, Eosine J, Eosine G-G, is usually the potassium salt of tetrabromofluorescein, $C_{20}H_6Br_4O_5K_2$, and of a yellow shade.

Eosine BN, Safrosin, is the potassium salt of dibromodinitrofluorescein, $C_{20}H_6Br_2N_2O_9K_2$, and belongs to the blue-shade eosines.

Erythrosine, Eosine J, is the potassium salt of tetraiodfluorescein, $C_{20}H_6I_4O_5K_2$; it gives very blue shades of vermilionettes.

Phloxine, Erythrosine B, and Phloxine T are bromo-chloro-derivatives of fluorescein, and yield blue shades of vermilionettes.

Rose Bengale is a very fine blue-shade eosine; chemically, it is the potassium salt of tetraiod-dichlor-fluorescein, $C_{20}H_6Cl_2I_4O_5K_2$.

To prepare vermilionettes or royal reds the method generally pursued is to diffuse the base, which may be either barytes or orange lead, or both, through water, to add the required quantity of eosine, and to heat the mass to about 160° F.; then there is slowly added, with constant stirring, a solution of lead acetate until all the eosine is precipitated out; lastly, the pigment is allowed to settle, and is finished in the usual way.

The following recipes for preparing several shades of these pigments exemplify the quantities of the materials used:—

VERMILIONETTES.

	No. 1 Pale. Lbs.	No. 2 Deep. Lbs.	No. 3 Deep. Lbs.
Barytes,	100	100	100
Orange lead,	30	30	...
Eosine,	2	6	8
Lead acetate,	6	16	20

ROYAL REDS.

	No. 1. Pale.	No. 2 Deep.
Orange lead,	100 lbs.	100 lbs.
Eosine,	4 ,,	8 ,,
Lead acetate,	10 ,,	20 ,,

The tint, as already noticed, will depend upon the chemical composition of the eosine which is used, while the depth of colour of the red will depend largely upon the quality of the make of eosine as well as upon the quantity of dyestuff used. By regulating the proportion of base to dyestuff many shades of vermilionettes and royal reds may be obtained, but, inasmuch as the eosine prepared by one maker greatly differs in quality from that of another maker, although professedly of the same chemical composition, it follows that the same shade of pigment may not be obtained from two makers' eosines. The proportion of lead acetate which is required to completely precipitate the eosine will also vary with the make of eosine used; it ranges from $2\frac{1}{2}$ to 4 times the weight of the dyestuff; colour-makers should always ascertain by a preliminary trial the precise amount required for any particular sample of eosine. When the pigment is properly made all the eosine is precipitated, and the wash waters are quite, or almost, colourless.

Instead of lead acetate, alum or alumina sulphate may be used; but the author considers that these are weaker precipitants and that they yield a pigment of inferior hue and permanence. The following recipes will show how these two salts may be used:—

VERMILIONETTES.

	No. 1. Pale.	No. 2. Medium.	No. 3. Deep.
Barytes,	100 lbs.	100 lbs.	100 lbs.
Eosine,	1 lb.	1½ lb.	3 „
Alumina sulphate,	3 lbs.	Alum, 10 lbs.	Alum, 20 „

A very fine pigment may be made as follows:—50 lbs. of barium chloride, 3 lbs. of eosine, and 50 lbs. of alumina sulphate are dissolved separately in water; the eosine solution is run into the precipitating vat, and then the other two solutions are run in simultaneously; the vermilionette precipitates almost immediately, and is finished in the usual way.

Properties of Vermilionettes and Royal Reds.—As pigments they are very brilliant in hue and have a good depth of colour, whether used as oil-colours or as water-colours, as well as good body or covering power. For colouring spirit-varnishes they are not good, as the eosine they contain is somewhat soluble in the spirit, and, consequently, the pigment loses its brilliant colour. One fault which they may have is that of blooming, due to the solubility of the colouring matter in the vehicle; this generally happens when insufficient lead acetate has been used to precipitate the eosine; in such cases the pigment usually contains some traces of free eosine, which passes into the vehicle and causes blooming.

They do not resist lengthened exposure to light and air; hence for work which must have permanence they cannot be recommended; still they will, if well made, stand a good deal of exposure, more especially if protected by a coat of varnish.

Vermilionettes and royal reds may be recognised by their greater or less solubility in alcohol, and by the solution showing a fluorescence, the character and colour of which will depend upon the particular eosine used in their preparation. Heat destroys the colour; if eosine and barytes alone have been used in preparing the pigment then the colour will be completely destroyed; but if orange lead has also been used then the residue will have a red colour. Nitric acid destroys the colour of these pigments. When orange lead is absent, then the colour is destroyed completely and at once; but if it is present, then the colour becomes darker and only disappears on boiling, and lead may be recognised in the solution.

SCARLET LAKES.—The number of scarlet and red azo-colouring matters is very great, and most, if not all, of them can be made to yield pigments. It is practically impossible to deal with all these, but the recipes which are given will serve to show the

lines on which to work to transform the azo- and acid reds into lake-pigments.

The azo-scarlets are sold under such names as scarlet G, scarlet R, scarlet 2 R, scarlet 3 R, scarlet 2 R J, Ponceau R, double brilliant scarlet G, crystal scarlet 6 R, &c. ; some of these names are common to several makers, but it does not follow that the scarlet G of one maker is the same product as the scarlet G of another maker ; hence it may happen that while the one dyestuff will be precipitated by alumina sulphate, the other may not be.

All the azo- and acid reds are not available for making lake pigments ; some yield very good lakes, others very poor ones. A few preliminary trials will show colour makers which are and which are not useful for this purpose.

For transforming the azo-colours, whether reds or yellows or oranges or other colours, four methods may be used ; one or more recipes illustrative of each method will be given, and from them the colour maker can readily see how to make other pigments than those here mentioned.

1st Method.—General method of making given on p. 269.

Bluish Scarlet.—100 lbs. of base, 3 lbs. of scarlet 2 R J, and 10 lbs. of barium chloride.

Scarlet.—100 lbs. of base, 5 lbs. of scarlet G, 20 lbs. of lead acetate.

Scarlet.—100 lbs. of base, 3½ lbs. of croceine scarlet M, 10 lbs. of lead acetate. A little ammonia completes the precipitation.

Deep Crimson.—100 lbs. of base, 20 lbs. of amaranth, 60 lbs. of barium chloride. A little addition of sodium carbonate completes the precipitation.

2nd Method.—Mix in the precipitating vat ½ lb. of eosine A, 5 lbs. of croceine scarlet M, and 33 lbs. of sodium sulphate (Glauber's salt). In separate vats dissolve 25 lbs. of barium chloride and 16½ lbs. of lead acetate ; when ready, run the barium chloride solution into the colour mixture, and then run in the lead solution. A very bright scarlet lake is thus obtained. This process may be applied to the preparation of lakes from two dyestuffs which require different precipitants.

3rd Method.—Very fine pigments can be made by the following process, which consists in dissolving in the precipitating vat 62 lbs. of Glauber's salt and 10 lbs. of scarlet R ; into this solution is run a solution of 70 lbs. of barium chloride ; the lake precipitated is finished in the usual way. By substituting for the scarlet R any other dyestuff which is precipitated by barium chloride other colours of lake pigments can be made.

Methods 2 and 3 yield very fine lake pigments, but they are more costly to make than those made by the general method.

4th Method.—100 lbs. of alumina sulphate are mixed with a solution of 25 lbs. of Ponceau RR, and the whole heated to about 60° C., when a solution of 100 lbs. of barium chloride is added; the whole is boiled and then allowed to cool down a little, when a solution of 60 lbs. of soda crystals is added. Care must be taken in making this addition, as excess of alkali will adversely affect the shade of the resulting pigment. The barium chloride and alumina sulphate react with one another, forming barium sulphate, which acts as the base of the pigment, and aluminium chloride, which remains in solution; this is precipitated on addition of the alkali in the form of alumina hydroxide, which combines with the dyestuff, thus forming the lake.

This method may be used with all colouring matters precipitated by alumina sulphate, and sometimes with others which are not so precipitated.

This process is not quite so good in its results as the second or third methods described above.

ORANGE LAKES.—Any of the azo- or acid oranges may be used to make lakes by any of the methods described under the reds. The following are three recipes for making orange lakes:—

1. 100 lbs. of base, 5 lbs. of orange G, 5 lbs. of barium chloride.
2. 100 lbs. of base, 3 lbs. of croceine orange, 4 lbs. of barium chloride, used according to the first method.
3. 62 lbs. of Glauber's salt, 10 lbs. of orange G, 70 lbs. of barium chloride, used according to method 3.

YELLOW LAKES.—The following recipes show the method of making yellow lakes from some of the azo- and acid yellows:—

1. 100 lbs. of base, 3 lbs. of yellow N, 10 lbs. of lead acetate.
2. 100 lbs. of base, 3 lbs. of Indian yellow, 5 lbs. of barium chloride, used according to method 1.
3. 62 lbs. of Glauber's salt, 10 lbs. of Indian yellow, and 70 lbs. of barium chloride, used according to method 3.

BLUE LAKES.—1. 100 lbs. of base, 2 lbs. of Victoria blue R, 5 lbs. of barium chloride.

2. 100 lbs. of base, 2 lbs. of alkaline blue, 5 lbs. of barium chloride.

3. 100 lbs. of base, 3 lbs. of alkaline blue, 4 lbs. of lead acetate.

There are many shades of alkaline blue, ranging from a very red shade 4R, to a very blue shade 6B, so that a great variety of tints or shades of lakes can be made; the proportions of colouring matter and precipitant given are only approximate,

and necessarily they will vary with the kind and make of alkaline blue used.

These recipes are used according to method 1, given under the red lakes.

4. 62 lbs. of Glauber's salt, 2 lbs. of alkaline blue, 70 lbs. of barium chloride, used according to method 3, described under red lakes.

BROWN LAKES.—1. 100 lbs. of base, 3 lbs. of orchil brown B, 6 lbs. of barium chloride.

2. 100 lbs. of base, 10 lbs. of cotton brown A, 20 lbs. of barium chloride. Both used according to method 1.

3. 62 lbs. of Glauber's salt, 10 lbs. of cotton brown A, 85 lbs. of barium chloride, used according to method 3. This gives a dark reddish shade of brown lake.

VIOLET LAKES.—1. 100 lbs. of base, 3 lbs. of acid mauve B, 15 lbs. of barium chloride. This gives a red shade of violet lake.

2. 100 lbs. of base, 3 lbs. of acid violet 6B, 10 lbs. of barium chloride. This gives a blue shade of violet lake.

Like the alkaline blues and the basic violets, the acid violets are made in a variety of shades, from a red 3R to a blue 6B, so that quite a large range of violet lakes, from a red to a violet hue, can be made from the acid violets.

Both these recipes are to be used as described under method 1 of red lakes.

3. 62 lbs. of Glauber's salt, 2 lbs. of acid violet 3B, 72 lbs. of barium chloride, used according to the third method.

BLACK LAKE.—100 lbs. of base, 10 lbs. of naphthol black B, 15 lbs. of barium chloride. This gives a rather grey shade of black.

GREEN LAKE.—100 lbs. of base, 5 lbs. of naphthol green B, 40 lbs. of lead acetate; the addition of a little ammonia completes the precipitation; the lake obtained is of an olive-green shade.

It is obvious that, in all the above recipes for making lakes from the acid coal-tar colours, by varying the proportions between the base and the colouring matter, a great variety of tints can be obtained from the same dyestuff; still, it is advisable not to reduce the proportion of dyestuff too much or the resulting lake will have too chalky an appearance. In this connection it may be mentioned that barytes makes the best pale-tinted lakes; china clay cannot be used very satisfactorily for this purpose, as, unless a large proportion of dyestuff is used along with it, it is apt to make chalky-looking lake-pigments. Necessarily, if the proportion of dyestuff to base be reduced, the quantity of precipitant required will also be less; the quantities of these

given in all the above recipes should only be taken as approximate; each particular sample of dyestuff will take its own proportion of precipitant, and as the actual quality of a dyestuff varies with different makers, it is scarcely possible to give very exact proportions, unless, of course, the maker's name were inserted, and this it is not deemed desirable to do in this book.

LAKES FROM ADJECTIVE COAL-TAR COLOURING MATTERS.

The third group of coal-tar colours are called the adjective or sometimes the mordant dyeing, dyestuffs, from the fact that, as already pointed out, they require the aid of a mordant, as it is called, to properly develop and fix the colour; in the most representative members of this group, alizarine, nitrosoresorcin, gambine, &c., the colour which is formed varies with the mordant used (see p. 250). Most, if not all, the dyestuffs which belong to this group possess acid properties, and have the property of combining with metallic oxides, like those of alumina, iron, chrome, tin, lead, &c., to form compounds which are more or less coloured, and quite insoluble in water; it is on this property that their value in dyeing, calico-printing, or in lake-making depends. In the two former arts the colour lake resulting from the combination of the dyestuff with the metallic oxide is formed on the fibre, while in the last it is formed in the free condition or on a base of some kind. The general principle which underlies the various processes for the preparation of lake pigments from this group of dyestuffs is that of bringing the dyestuff into contact with the oxide of the metal with which it is desired to combine it, and thus cause the colour lake to be formed.

The principal colouring matters of this group are alizarine and purpurine; these two bodies are sold under the general name of alizarine, which is made in several brands distinguished by letters, AB, SX, V, G, &c. Practically, there are two kinds of alizarine—yellow alizarine, which, with alumina, gives scarlet reds, and consists principally of alizarine; the other kind is the blue alizarine, which, with alumina, gives more crimson reds than the last, and consists mostly of purpurine. Then there are alizarine blue, alizarine yellow, alizarine cyanine, gallein, gallocyanine, galloflavine, nitrosoresorcin, gambine, &c.

ALIZARINE LAKES.—Various processes can be employed for converting alizarine into lakes.

1. **Pure Alizarine Lake.**—Mix 20 ozs. of ordinary commercial

alizarine* with $1\frac{1}{2}$ galls. of water; then add 10 ozs. of alumina sulphate previously dissolved in water, and 2 ozs. of calcium acetate dissolved in water; boil the whole together for about an hour; then add 10 ozs. of soda crystals dissolved in water in small quantities at a time, at intervals long enough to allow of the subsidence of the effervescence thus set up. The whole mass is now boiled for about an hour, then allowed to stand for 24 hours, filtered, washed, and dried. This makes a dark red lake of good body and staining power. The shade or tint will depend upon the kind of alizarine used. Excess of soda crystals should be avoided, as it causes the lake to be of a dark colour.

2. **Dark Red Alizarine Lake.**—Diffuse 100 lbs. of barytes through 50 gallons of water, add 20 lbs. of alizarine, 10 lbs. of alumina sulphate, and 2 parts of calcium acetate; stir well together, and then allow to stand for two or three hours, stirring at intervals to keep the ingredients well mixed. Heat slowly, so as to take about two hours to reach the boiling point, and, at intervals, add portions of a solution of 10 lbs. of soda crystals. Much of the beauty of the resulting lake depends on the care exercised during this stage of the process; too rapid heating, and too rapid addition of the soda crystals, has a tendency to cause the shade of the lake to be darker than it should be. The lake obtained by this process is of a fine ruby red colour. After it is formed, as described above, it is finished in the usual way.

3. **Alizarine Lake.**—Diffuse 100 lbs. of barytes through 50 gallons of water, add 10 lbs. of oleine or Turkey-red oil, and boil for one hour; allow to stand for twenty-four hours, stirring up at intervals, add 20 lbs. of alumina acetate (12° Tw.), and 2 lbs. of calcium acetate, stir all well together, and allow to stand for two days; then boil well for two hours, adding at the same time 5 lbs. of soda crystals. When the lake has formed, filter off, wash, and dry.

4. **Alizarine Red Lake.**— $6\frac{1}{2}$ lbs. of alumina sulphate are dissolved in water, and to this solution one of 1 lb. of calcium chloride is added; a precipitate of calcium sulphate is obtained, but, before this has had time to settle out, a solution of $4\frac{1}{4}$ lbs. of soda crystals is added; the precipitate of alumina and calcium sulphate thus obtained is collected on a filter and washed. It is

* Nearly all the so-called alizarine colours are sold in the form of a paste, containing about 20 per cent. of actual colouring matter. The reason for this form is that, as a rule, these dyestuffs are insoluble in water, and it has been found by practical experience that if sold in a dry form that the dyestuff does not mix well with water, and that they thus give rise to uneven dyeing, while the paste form mixes very well with water, and uneven dyeing rarely occurs.

then introduced into a solution containing 3 lbs. of alizarine, 1 lb. of Turkey-red oil, and $1\frac{1}{2}$ oz. of tannic acid, and the mixture heated for half an hour to about 70° C., when it will be found that the alumina has taken up all the alizarine, and become dyed thereby. It is now boiled for one hour longer, and then finished in the usual way.

5. **Alizarine Red Lake.**—Muller Jacobs has patented, in Germany, the following process for making an alizarine lake:—50 grammes of alizarine oil are dissolved in 1,400 cc. of water, 15 grammes of alizarine, and 0.2 grammes of tannic acid; the mixture is heated to boiling, when 60 cc. of a solution of alumina sulphate of 1.1014 (20.3° Tw.), specific gravity, which has been previously mixed with 22 per cent. of soda crystals, are added. The lake soon forms, especially on boiling for some time; it contains some oil which can be extracted with ether. The use of such a large proportion of oil is objectionable, as it makes the resulting lake very greasy, and prevents its use for certain purposes. Moreover, it is not practicable on a commercial scale, owing to the cost involved in extracting this excess of oil.

In making alizarine lakes it is important to use an alumina sulphate which is free from iron, as this latter ingredient has a great and deteriorating influence upon the colour of the resulting lake; very small traces of iron are sufficient to give a brown hue to the lake.

The methods of making lakes from alizarine, just described, are equally applicable to the preparation of lakes from the other alizarine dyestuffs.

SCARLET LAKES may be made from a mixture of alizarine and alizarine orange.

YELLOW LAKES can be made from alizarine yellow, galloflavine, gambine yellow, and flavazol, by any of the above processes, using alumina salts as precipitants. Generally a very satisfactory lake, of good colour, can be readily obtained from any of the dyestuffs named.

ORANGE LAKE can be made from alizarine orange, or by using a mixture of alizarine and one of the yellows just named.

MAROON or **CLARET LAKES** can be obtained from alizarine, by substituting acetate of chrome for acetate of alumina, in process No. 3 above.

BLUE LAKES can be obtained from alizarine blue, alizarine cyanine, or chrome blue, by using chrome acetate as a precipitating agent, and the process described in No. 3 of alizarine lakes.

GREEN LAKES can be made from nitrosoresorcin and

gambine by using iron sulphate as the precipitating agent; the lakes from gambine are rather brighter than those from the resorcin product. Dark green lakes can also be obtained from coerulein by using chrome acetate as the precipitant.

VIOLET LAKES can be made from chrome violet by using chrome acetate as the precipitant; or from gallein and gallocyanine, by using either chrome or alumina salts as precipitants.

BROWN LAKES can be made from anthracene brown with chrome acetate as the precipitant.

It has not been thought needful to give full details of the method for converting all the alizarine colours into lakes, as the process or processes, and the proportions of materials used are very similar to those which are used for making alizarine lakes, and these have been fully dealt with. Any intelligent colour-maker can easily apply the proportions and process for making an alizarine red to making an alizarine blue-lake.

The great merit which distinguishes the lakes made from the alizarine group of dyestuffs is that of being permanent; they resist a considerable amount of exposure to air and light without becoming faded or dull, they can, therefore, be used for decorative or artistic purposes where some degree of permanence is essential; still, even in this property, they are by no means equal to such pigments as vermilion or yellow-ochre or chrome-yellow.

CHAPTER X.

ASSAY AND ANALYSIS OF PIGMENTS.

BESIDES the analysis required for ascertaining the chemical purity of a sample of a pigment, it is also necessary, with many of the pigments, to make an examination or assay for other properties—such as colour or hue, brilliancy, colouring power, covering power or body, durability, fineness, and what may be called miscibility. In some pigments they are fairly constant in degree, while in others—such as the chromes, ochres, umbers, blacks, &c.—they are very variable, hence due precaution should be taken, both by purchasers and makers, that every lot of pigments is uniform, both in quality and intensity.

1. **COLOUR** or **HUE**.—The tint or shade of a pigment is a matter of the greatest importance. The terms, as used by colourists, are, however, rather confusing; thus some persons consider tints to mean the standard colour mixed with white so as to obtain lighter colours; shades they consider to be those produced by mixing the standard colour with black; while other persons use these terms as if they were synonymous, and speak of the shade or tint of a colour without any reference to a standard. This, perhaps, is the custom more particularly in the dyeing trades. Under these circumstances it will be best to use a term which is free from any liability of confusion, viz., “hue.” The hue of a colour may be defined as the optical effect produced on our colour-sense by a pigment.

The hue of a pigment is a variable quantity; in some cases, such as vermilion and antimony orange, where the chemical composition is a definite one, and does not vary with different makers and batches, the hue only varies within small limits. In other cases, such as the chrome-yellows, Brunswick greens, and many others, where the composition is liable to vary with different makers, and even with different batches of the same maker—as also the ochres, umbers, and other natural pigments—the hue varies very much. In such cases, the terms—pale,

medium, dark, &c.—are arbitrary distinctions which are by no means uniformly indicative of the same precise intensity of hue. Hence, in all such pigments, special examination is required in order to determine what the actual intensity is.

The assaying of a pigment for hue can be done in two ways—comparatively or absolutely; the former is the one usually adopted.

Comparative Method of Assaying Pigments.—In this method the hue of a sample is simply compared with that of a standard sample and the results stated in terms of this standard. For this purpose a sample of the best quality is selected, and a fair quantity of it is placed in a bottle. Colours which are acted on by light, such as the chrome-yellows, Brunswick-greens, and others, are placed in orange or amber coloured bottles to protect them from such action; while white pigments, black pigments, ochres, umbers, and the permanent colours generally, are kept in ordinary bottles. These samples form the standards.

The method of assaying the hue of a pigment by comparison with a standard sample is simple, but experience and a good eye for colour are essential requisites; some persons can detect very small differences in the hues of pigments, while others are deficient in this respect, and consequently do not make good assayers of hue. The colour sense can be improved by cultivation.

A sheet of black paper for pale colours, or of white paper for dark colours, is placed in front of a good window and in diffused light, this being the best for assaying hue. The paper must have a dead surface, as a bright one interferes with the observations too much. A small heap of the standard colour is placed on the paper by means of a palette knife, and beside it a similar heap of the colour to be compared; then, by a gentle but steady downward pressure with the knife, the surfaces of the two heaps are flattened in such a way that a distinct line separates the two colours; if the knife is moved at all laterally, the two heaps of colours are partially amalgamated, and a perfect comparison thereby precluded. The observer now carefully compares the two heaps of colour; this should be done in several ways, viz., by looking down on them, by holding the paper on a level with the eyes and looking sideways at the colours, &c.; by this means and with a little experience the differences in the hue of colours can be readily observed.

There are two points in connection with the hue of a colour which can thus be compared with a standard colour: 1st, depth; 2nd, tone. The two samples being compared may be equal in

depth of hue or colour, yet different in tone. For instance, in two vermilionettes, the standard sample may have a bluish tone, while the sample compared with it may have a redder tone. Again, two samples of chrome-yellow when compared together in this way may show differences of tone; one may be a greenish-yellow, while the other may have an orange tone. These differences in tone are of quite as much importance as differences of depth of hue, as occasionally they will have an influence on the use of a pigment; thus, an orange-toned chrome-yellow does not mix with Prussian blue to make greens as well as a greenish-toned chrome-yellow does.

Absolute Method of Assaying Hue.—An absolute method of assaying pigments for hue may be founded on the use of an instrument devised by Captain Abney, named by him a "colour patch" apparatus. It is described in his book on *Colour Measurement and Mixture*. This method, while of some interest from a scientific point of view, is, however, scarcely one which will come into practical use in a colour shop, owing to its rather complex construction and to its requiring powers of experimenting beyond those of colour-makers generally. However, a brief description of the process and apparatus may be useful. The colour patch apparatus consists, first, of a spectroscope, with which a spectrum of the light from an arc electric lamp can be formed on the screen of a camera; by substituting a slide having a narrow slit in it for this screen and passing the light which comes through this slit through a lens, a patch of coloured light can be obtained on a screen placed behind the camera; the colour of this patch will depend upon the position of the slit in relation to the spectrum which falls upon it and will necessarily be monochromatic. The arc electric lamp is preferred as the source of light, because it can be more depended upon than any other kind of light for uniformity in amount and quality, which feature is of importance where light measurements have to be made.

Another part of the apparatus consists of an arrangement by which a disc of coloured card can be rotated; the same apparatus also carries a larger pair of overlapping black and white discs, the amount of overlapping being capable of variation at will. This is placed so that the colour patch falls partly upon the coloured disc and partly upon the black and white discs; these are rotated, and the slit of the colour patch apparatus moved along the spectrum until a point is reached when the luminosity of the patch on the two discs is equal. Then a note is made of the position of the slit, as given on a scale attached to the colour patch apparatus,

and also of the relative quantity of black and white exposed in the black and white discs; then another trial is made in the same way, only that the black and white discs are altered so that a different proportion of the two colours are exposed. It will now be found that equal luminosity of the colour patch on the discs occurs when the slit is in a different part of the spectrum to what it was before the two measurements were made. These measurements are repeated for various proportional exposures of the black and white discs. Then on a chart is drawn two sets of lines, viz., a horizontal set, to show the proportions of black and white; and a vertical set, to show the position of the slit on the spectrum. Then by drawing a line through the points given by the various readings, a curve is obtained indicating the reflecting power of the particular pigment experimented with in each part of the spectrum.

By carrying out this system with different pigments we are able to see how one compares with another.

By a modification of the experiment the light reflected from a surface painted with a pigment can be compared with that which is reflected from a surface painted with a standard sample of the pigment. If instead of laying down the curve on a chart, it is drawn on a sector of a circle, so that the scale of the spectrum is measured off along a radius and the relative intensities on concentric circles, then a curve of somewhat different shape is obtained. If this be cut out it forms a colour template which, when revolved in front of the spectrum formed in the apparatus, cuts off just enough light that the remainder forms a colour patch of the same hue as the colour pigment; by causing a patch of colour to be formed side by side with the colour patch, the relative hues may be accurately compared together. This second patch of colour is obtained by reflecting from a surface painted with the pigment. By making templates in this way and using the colour patch apparatus in the manner indicated, there is a certain method of comparing hues of pigments.

BRILLIANCY or LUMINOSITY.—This is an important feature of pigments, and one in which different makes of the same pigments are rather liable to vary. As with hue, brilliancy is assayed by comparison with a standard sample, and this can be done in precisely the same manner as described for hue.

COLOURING POWER.—Colouring power is that property of pigments which enables them to give colour to surfaces and to other pigments. As explained in another place, pigments possess two properties available for paint making, viz., colour and body, or covering power (see below). Some pigments are

used almost solely on account of their colour, as, for instance, carmine, Prussian blue, ultramarine, vermilionettes; hence with these strength of colour or colouring power is an important feature. Other pigments are used solely on account of their covering power, and then colour is immaterial.

Colouring power is tested also by comparison with a standard sample. In principle it is done by ascertaining how much of another pigment it will colour to a given depth.

Supposing it is a sample of vermilionette whose colouring power is to be determined, then 10 grms. of the sample are weighed out and mixed with 30 grms. of china clay; the mixing must be thoroughly done. 10 grms. of the standard sample are mixed in the same way with 30 grms. of the same sample of china clay. The two mixtures are now compared together for depth of colour as described above; if the two samples are equal in colouring power, the depth of colour of the two mixtures will be the same; if one is stronger than the other, then one of the mixtures will be darker than the other. Some idea of the relative strength of colouring power may be obtained by adding small and known weights of china clay to the darkest sample until the tint of the mixtures are equal to one another; then the samples have a colouring power proportional to the amount of china clay used; thus, if one sample took 30 grms. of china clay and the other sample 37.5 grms., then the relative colouring power is as 30 to 37.5; or, if the strongest sample be taken at 100, then the colouring power may be expressed in percentages thus, 37.5 : 30 :: 100 : 80; the weakest colour has only 80 per cent. of the colouring power of the strongest.

As the toning colour for all pigments except whites a good sample of china clay may be used; gypsum also makes a good toning colour; barytes and white lead are a little too heavy. For whites a good animal black makes a good toning colour.

When a large number of assays for colouring power have to be made a standard tint should be made by taking, say, 50 grammes of the standard sample, and mixing with about twice its weight of the toning colour; this tint may be used in subsequent tests, and will save some time in the preparation of a standard tint. It is important, however, that the same sample of toning colour be used to mix with the samples, whose colouring power is being tested, as has been used in making the standard tint.

COVERING POWER or BODY.—This is a most important property of pigment—perhaps the most important, for those which possess it in the greatest degree are universally considered to be the best pigments. It may be defined to be the power of

covering over or hiding the surface of any body on which it may be spread when mixed into a paint. Some pigments, such as crimson lake, Prussian blue, and barytes, are deficient in this property; others, such as white lead or the chromes, possess it in great degree. In the same pigment, however, the covering power is liable to vary to a greater or less extent. To some extent the covering power is dependent upon the condition of the pigment: if this is of an amorphous character, without any definite form of its own, and is opaque, it will, as a rule, be found to have good covering power or body; on the other hand, if a pigment is of a transparent character, and is crystalline in its structure, then its covering power is liable to be small. Sometimes a pigment may be obtained in both conditions, according to the particular circumstances under which it is made; thus, lead chloride may be obtained as a white amorphous powder, or in small transparent crystals. In the former condition it may be used as a pigment, as it has some covering power; on the other hand, the crystalline variety is useless as a pigment, as it has no covering power at all.

Unfortunately it is by no means an easy matter to devise a method of assaying the body of pigments; it cannot be expressed in absolute figures as can chemical composition, at the most it can only be assayed in a comparative manner as is colouring power.

The best plan for assaying the covering power or body in pigments is to place 2 grammes of the standard sample and of the pigment to be compared with it on a black porcelain tile, and to add 3 grammes of oil to each; the oil and pigment are thoroughly incorporated by means of a palette knife, and then each is spread over the plate in a layer, making each layer of paint of as uniform a thickness as possible. That sample which, when thus made into a paint and spread over the tile, most completely obliterates the surface of the latter has the most covering power. It is possible to obtain some idea of the comparative covering power of two samples by this method. To that sample which has the most body a small additional quantity of oil is added, and the body of the mixture again compared with the other sample; if it is still the best more oil is added, and the process repeated until both samples appear to have the same covering power. Now, it may be assumed, without much error, that the covering power or body of the two samples is in proportion to the quantities of oil used to mix with them; that sample taking the most oil having the most body. Thus, of two samples of barytes one took 3 grammes of oil, and the other 3.25 grammes;

taking the last as the standard or 100, the former had only $3.25 : 3 :: 100 = 92.3$, or 7.7 per cent. less body than the standard sample. Or, to put it in another way, $3 : 3.25 :: 100 = 108.3$; that is, 100 lbs. of the standard sample will cover as much surface as 108.3 lbs. of the other, weaker sample.

DURABILITY or PERMANENCE.—Durability is one of the most important properties a pigment can possess, for upon it depends the fact whether it will ever come into extensive use as a pigment, especially for artists' use, where permanence is one of the most essential things a picture must possess. Until recently our knowledge regarding the permanence of pigments, or, what is the same thing, their power of resisting exposure to light and air, was empirical and unreliable; but recent researches on the subject have quite altered its character.

Of those colours which have been shown to be permanent, the mineral pigments—ochres, umbers, sienna, Vandyke brown, barytes, Chinese white, siennas, ultramarine, vermilion, Prussian blue, and some others—are the most important, and can safely be used on work which is required to have great permanence.

What is frequently sold under the names given to old pigments is, however, not always what it ought to be, being more or less adulterated with an inferior pigment; it is, therefore, advisable to test a sample, not only for purity, but also for durability, as the adulterants are frequently anything but permanent.

Of late years many new pigments have been placed on the market, which have been made from coal-tar colours; unfortunately, many of these, although of brilliant hue, are far from being permanent, and will not resist any lengthened exposure to light and air. It is desirable that a user of these pigments should make some experiments as to their durability. There is a great deal of difference in this respect among these coal-tar pigments. Some are as permanent as can be wished; others, again, are very fugitive. Then, again, the method of using has more influence on the durability of these pigments than it has on that of the older pigments; for some which are rather fugitive, when used as water-colours, will resist a fair amount of exposure when used as oil-colours.

Probably the simplest method (which is a very good one) of testing the durability of colours, is to provide a sheet of unglazed cardboard; that known as Bristol board will do very well. It must have so slight an absorbent property that if any coat of paint is placed on the surface it will remain there, and not soak into the substance of the cardboard. This sheet of board

is ruled into squares or rectangles, measuring about 3×2 or 2×2 inches.

A little of the colour to be tested is ground up with a little gum water into a smooth paste, and a portion of one of the ruled spaces on the cardboard painted with it. It is advisable to rule and prepare two sheets at the same time. The name of the colour can be written either underneath the patch of colour in the square, or in a corresponding position on the back of the card. It is also advisable to grind a little of the pigment with oil, so that the relative durability as a water-colour and as an oil-colour can be tested.

One of the prepared cards is hung in a place where it is exposed to as much sunlight and air as possible, while the other card is placed in a drawer away from any such influence. After a week or two of exposure the cards can be compared to see if any changes have occurred; they can then be replaced in their respective positions, and from time to time are compared together. Any change which may have been brought about by the action of sunlight and air on the exposed card will be observable; some colours will be changed in a few weeks' exposure, other colours require months of exposure to produce any effect.

By placing a card painted in the manner described with different pigments in a closed cupboard, in which is placed a vessel containing some ferrous sulphide and dilute sulphuric acid, the action of sulphuretted hydrogen on the colours can be tested; if any are affected by this test it is certain that they will be similarly affected when exposed to the action of impure air.

Testing pigments for durability is a very long operation, and it is no wonder that there have been few systematic researches on this subject. The most exhaustive and systematic experiments on the permanence of pigments which have ever been made are those made by Captain Abney and Dr. W. J. Russell, at the request of the Science and Art Department; these extended over a period of two years, and the results were published in the form of a Blue Book, entitled—"Report on the Action of Light on Water Colours." This report must be consulted for details as to the method of testing adopted, &c.; but the following will give some idea of the methods and results of these researches.

The experiments were carried out as follows:—A sheet of Whatman paper of good quality was covered with washes of the pigment to be tested in such a manner as to form a series of eight tints, varying from pale to dark. From this sheet, strips, 8 inches long by 2 inches wide, and containing all the tints,

were cut, and two of them placed in a glass tube, 2 feet long and $\frac{3}{4}$ inch in diameter, open at both ends, and bent over at the upper end in the form of a hook, in order to prevent the admission of dirt; the tube was then hung in such a place as to receive as much sunlight as possible. It may be mentioned that one of the strips of paper was covered with oil-cloth so that it could not be acted on by light, although otherwise it was subjected to the same influences as the other strip. Similar tubes were filled with dry air, moist air, moist hydrogen, while one set had the air withdrawn so that the strips were exposed in a vacuum. The experiments lasted from May, 1886, to March, 1888. The results of these experiments are given in the table opposite, which has been compiled from the tables given in the Report.

Prussian blue fades when exposed to light, but on placing the faded colour in a dark place the colour comes back again.

It is evident from the above experiments that moisture has a material influence on the durability of pigments; colours which fade in moist air are permanent in dry air; then, again, colours are more permanent in an atmosphere of moist hydrogen gas and in a vacuum than in air; it is evident, therefore, that the three elements of destruction which cause colours to fade are light (which may be called the determining cause), oxygen, and water. But light alone has little effect. Hence it may be concluded that when a colour is kept under conditions where moisture and air can have little action it will be permanent; so that it should always be kept under such conditions if possible.

MIXABILITY.—This is a term which the author has introduced in connection with pigments to express the power of pigments to mix more or less readily with oil or other vehicles or other pigments. It is a most important property, and much of the value of a body when used as a pigment depends on it; some pigments do not readily mix with oil, while some of the modern pigments made from coal-tar colours seem to have the property of retarding the drying of the oil, therefore they cannot be said to mix well with it. Then, again, in mixing pigments together to produce compound tints or shades, there are some pigments which can be mixed with all others without any ill effect being observed; on the other hand, some pigments can be mixed with a few others without any change occurring, but when mixed with others some action of a deteriorative character will take place.

To test pigments for the property of mixability, the best method is to provide a sheet of cardboard of not too porous a character, and to rule this into squares of about 2 inches each

way. A little of a pigment is rubbed with a small quantity of linseed oil in a white basin, during which operation its behaviour with the vehicle will be noticed; it should be observed whether it mixes freely with oil or shows a tendency to separate out; this latter effect may be due in most cases to the pigment not being thoroughly dry. A little of the mixed pigment is now rubbed in one of the squares of the card. Then prepare mixtures of the pigment with other pigments—white lead, whiting, Prussian blue, emerald green, yellow chrome, vermilion, lamp-black—rubbing the pigments together with a little gum-water; these mixtures are rubbed on the card. When all the mixtures are ready the card is exposed to the air, and to diffused daylight only, for some time, say two or three weeks. After two or three weeks' exposure, the card may be examined and any effect of change of colour noted; during the interval observations should be made as to the drying of the oil in the first square to see whether the pigment has any influence of any kind, either in retarding or in facilitating the drying; the former case will show that the pigment is not suitable to be used as an oil-colour, although it may be perfectly suitable as a water-colour. The other squares will show the action of one pigment on another; those which exhibit no alteration in shade or tint beyond, perhaps, a little fading will show the pigments which may be mixed together without any effect upon one another; while those which have altered will show the observer what mixtures to avoid.

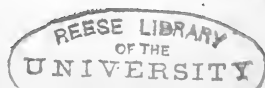
FINENESS.—The quality of a pigment is a feature which is more or less dependent upon the size of its particles, the smaller these are (or, in other words, the finer the pigment has been ground or produced in the process of manufacture) the better will it be as a pigment; its body or covering power will be increased, its colouring power will also be improved and its tone brightened very considerably; therefore, it may be laid down that the finer a pigment is the better it will be for use in painting.

It is by no means easy to make a practical test for the fineness of a sample of pigment. By rubbing between the fingers it is possible to make a rough comparative examination, but no accurate results can be arrived at by this means; when the quality of two samples is very similar this rough test cannot be relied on. By spreading a little on a plain microscope slide and examining it through a powerful microscope, using, say, a $\frac{1}{4}$ -inch objective, some idea of the relative fineness of two samples may be obtained. Another method of testing which will give more reliable information and better comparative figures than the tests just noted is the following:—Weigh out about 5 grammes into a

mortar, and grind, without much rubbing action, into a smooth paste with water; then transfer this to a tall cylindrical graduated measuring glass, and rinse out the mortar with water, so as to get the whole of the material into the glass; fill this up with water to the top mark, and, putting in the stopper, shake well for a few minutes; then place on one side; the particles will gradually settle, and the time it takes for the water to become clear up to, say, the half-mark should be noted. If this be done with a number of samples a series of figures will be obtained which may be taken as showing the comparative fineness of the various samples, for the rate at which the material settles depends upon the fineness of its particles; the finer these are the slower is the action, while the best samples are characterised by subsiding most slowly. Then this test will also show whether the sample is of uniform quality or whether it contains both coarse and fine particles; in the former case the rate of deposition will be uniform, while in the latter case the larger particles will settle out very rapidly, leaving the finer particles to subside more slowly. For example, the author tested three samples of china clay by this method. Sample A took 60 minutes to settle out; sample B 44 minutes; while the coarse part, forming the great bulk of sample C, settled out in 30 minutes, and the finer remainder in 90 minutes. A and B were uniform in quality, but sample A was superior to B, being composed of the finer particles. Sample C was of mixed quality, containing both coarse and fine particles; the former settling out rapidly, the latter more slowly. C would not be so good as B for many purposes.

This test cannot be used for examining the fineness of samples of different pigments: thus, for example, the comparative fineness of a sample of white lead and of barytes cannot be ascertained by its means; only different samples of the same pigment can be compared together. This arises from the fact that the specific gravity of a body has a great influence on the speed with which its particles will fall when placed in water, and as there is a great difference in this respect between different pigments, it follows that a sample of white lead will settle out much quicker than a sample of china clay, although both samples may be equal in fineness of powder.

The method of testing the fineness of the particles of a pigment here given is possibly not a perfectly accurate one; but still some very useful information as to the quality of a pigment may be obtained by its means, and it does not need any elaborate apparatus to carry it out.



CHAPTER XI.

COLOUR AND PAINT MACHINERY.

IN making colours or pigments, and in preparing them for use in painting, and in making paint, there are a good many mechanical operations which are common to all pigments and all paints. Upon the care with which the various mechanical operations, such as precipitating, drying, grinding, &c., are carried out, depends much of the quality of the pigment or paint, especially as regards its brilliance and covering power. The machinery for carrying out these various mechanical operations forms an important part of the outfit of a colour- or paint-shop. In the present chapter it is proposed to discuss the various machines which are required to carry out the various processes involved in making a pigment and its conversion into a paint.

LEVIGATION.

In the preparation of such natural pigments as the ochres, siennas, umbers, china clay, and barytes for use in paint-making, levigation plays an important part. These bodies as they are found in nature contain a good deal of gritty matter and other impurities, from which they must be freed before they are of use in paint-making; there is no better process for this purpose than levigation.

The principle of the process of levigation depends upon the fact that when fine particles of a comparatively light material mixed with coarser particles of the same material or with particles of a heavier material are agitated with water and then allowed to stand, the coarser and heavier particles will fall first, while the lighter particles will form a layer on the top of the coarse particles, which can thus be separated from the fine particles. A modification involving the same principle is where the mass of material is subjected to the sifting action of a current of water, the strength of which suffices to carry the fine particles only into a tank, where they are allowed to subside. China clay

is an example of the preparation of a pigment in this way (see p. 84).

Should the raw material be made up of several distinct kinds of particles—very fine, fine, medium, and coarse, as in the case of some ochres—it is possible, by means of levigation, to separate them into their various constituents. By so arranging the current of water that it runs through a number of tanks with varying rates of speed, the coarse particles will be left in the first tank, the medium particles in the second tank, the fine particles in the third tank, and the very fine in the fourth or last tank.

It will be seen that levigation, while effective, is a very cheap process; for it only requires a cheap material, water, and the cheapest kind of colour plant, tanks, for carrying it out.

The details of the plant required or used in levigating at any particular works depends upon many factors, such as the position of the works, whether situated in the centre of a town, in a wide valley, or on a hill side. The facilities for obtaining the requisite supply of water is also a factor in determining the arrangement of the plant.

In Fig. 28 is shown in plan and elevation a plant suitable for

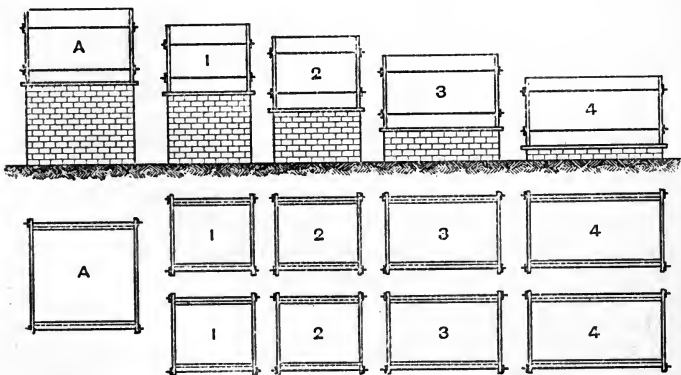


Fig. 28.—Levigating plant.

levigating ochres, umbers, &c. It consists of 9 tanks, 8 of which are arranged in 2 series of 4, while the ninth is an odd tank. Another good arrangement would be one of 10 tanks, 9 arranged in 3 sets of 3, the tenth being an odd one.

In the odd tank, A, the crude material is thoroughly mixed with water; in Cornwall, Derbyshire, and a few other mining

districts, this tank is known as the "buddle;" in this the very heavy stuff remains while the current of water, which is continually passing through, washes away the finer particles. From the buddle the water flows into the first settling tank 1; this being large, the current becomes retarded, and some of the material it contains settles out; from tank No. 1 the water flows into tank No. 2; this is made, or should be made, rather larger than tank No. 1, so that the current being spread over a larger surface becomes slower, and, therefore, has less force, thus allowing the finer particles to settle out. From No. 2 the water flows to No. 3 tank, which is larger still; and, finally, to No. 4 tank, which is yet larger, so that very fine particles of pigment can settle out; when tank No. 1 is full the current from the buddle is diverted into the second series of tanks, while the colour or pigment in the tanks of the first series is settling out; when this is completed the water in these tanks is run off, and the pigment dug out, when the tanks are ready to be filled again. By having a set of four settling tanks, four qualities of ochres, or siennas, or umbers, may be obtained. When the second series of tanks are full, the current is again sent through the first series. By having three series a more perfect system can be adopted; the current of water is sent through the first series until these are full, then through the second series while the material in the first is settling out; when the second is full, the current is diverted to the third series; by this time the colour in the first will have settled out, and can, as explained above, be collected; when the first lot of tanks are emptied of their contents they are ready to be refilled by diverting the current from the third set of tanks. Thus the three operations of filling, settling, and emptying can go on concurrently in a complete manner.

The tanks should be arranged, as shown in the drawing, one above the other, so that the water can run from one to the other; and the last tank of the series should be of such a size that it will take a day to fill it.

In ultramarine-making, where levigation forms an important part of the finishing process, the last tank is either made very large or a large number of small ones are provided, as the fine ultramarine takes a week to settle.

When space is available it is a good plan to have a set of large storage tanks; into these is thrown the wet pigment taken out of the settling tanks, and here it remains for some time; a further settling takes place, and the pigment becomes drier; this effects an economy of both time and fuel in the complete drying during the final stage. This saving of fuel is a matter of some import-

ance in dealing with such cheap natural pigments as china clay, umber, &c.

The strength of the current of water is a matter that requires attention; if too strong, it will carry over some of the coarse material from the buddle to the settling tanks, and will prevent the fine material from settling in the end tanks; on the other hand, too gentle a current will not extract the whole of the valuable material from the crude stuff in the buddle; this is a detail which the operator can easily arrange.

If only small tanks are required they may be made of wood; large tanks may be built of stone flags, or of brick, if flagstones of sufficient size are not available. If bricks are used the inside of the tank should have a smooth surface, so as to facilitate the ready removal of the colour which has settled out. In any case arrangements should be provided for running off the clear top liquor from the settled pigment; this may be done by providing in each tank a set of holes kept stopped by plugs, which are removed when it is desired to run the water away. Or the water may be syphoned off by means of syphons provided for that purpose.

The amount of water required to levigate a pigment is a variable amount, depending on the nature of the sample of colour under treatment and on the plant used, so that no definite rules can be laid down.

The size of the tanks can be varied to suit the required output of colour, and is a point which every colour-maker must settle for himself, remembering, first, the deposited colour will contain about half its weight of water, and will therefore be heavier than the dry material; second, that the total volume of the tanks must be much larger than that of the material which settles out from them. Another point is to make the tanks sufficiently strong to bear the pressure of the water, &c., they contain, which is great; thus a tank, 20 feet long \times 5 feet broad and 4 feet deep will hold $20 \times 5 \times 4 = 400$ cubic feet of water, or 400×62.35 lbs. = 11.13 tons, which is the pressure exerted by the water on the bottom of the tank.

In some cases, before levigating, the material is ground, and in such cases the grinding is usually done under water; for this purpose special mills are made, descriptions of which are given further on.

DRYING OF PIGMENTS.

After a colour has been prepared for use as a pigment by the process of levigation, as just described, or by that of precipitation,

described below, and also by other processes, it is in a wet condition, probably containing from 25 to 50 per cent. of water, according to its nature. If required in what is known as the pulp state, in which condition it is used by paper-makers and stainers, no further treatment is necessary; but, if required to be used in the preparation of paint, it is absolutely necessary that it be dried, otherwise it will not mix with the oil used in the manufacture of the paint.

The drying of pigments is carried on in what are called "drying-stoves;" these are usually nothing more than brick chambers with solid walls on three sides, and a door on the other, covered with a roof; round the bottom of three sides runs a horizontal flue belonging to a furnace which can be fed from the outside. The wet colours are usually placed in shallow, flat, earthenware pans, which are placed in piles one above another, and then left in until they are dry. This is by no means a satisfactory method, the piling of the pans, one above another, and the absence of any system of ventilation beyond accidental cracks in the door and walls, tend to keep the atmosphere of the stove saturated with steam, and to check the drying operation.

A better plan is shown in Fig. 29; it consists of a brick chamber built of any convenient size; as before, the flue, F, of a furnace runs round the bottom; the sides of the flue are built of brick, the top of flagstone, and the fireplace, E, is placed outside the chamber. Instead of such a flue, steam pipes may be used for heating it. Above the flue or steam pipes, is a staging, S, forming a false floor, on which is erected a framework, C, C, C, C, of iron or wood forming skeleton shelves on which the pans of wet colour are placed. These shelves support the pans a small distance apart from one another, and so allow free egress for the water-vapour which comes from the colour. A constant current of warm air, generated by a fan or air propeller, is continually flowing over the pans of colour and out through the ventilator, V, in the roof of the stove, thereby carrying off the water-vapour as fast as it is given off from the wet colour. It should be borne in mind that the colour, just as it comes from the filters or presses, may contain from 25 to 50 per cent. of water; if, by any means, this water is prevented from escaping from the colour, then the drying is retarded; or if it is prevented from readily escaping from the stove, it is liable to condense on the inside of the roof, and to fall down in drops on to the colour below. In some cases, *e.g.*, chrome-yellows, these drops are apt to produce spots on, and discolouration of, the pigment which is being dried. The more freely the water-vapour can escape into the atmosphere

the less chance there is of such mishaps occurring. D is a door for filling the stove, and G, G skylights.

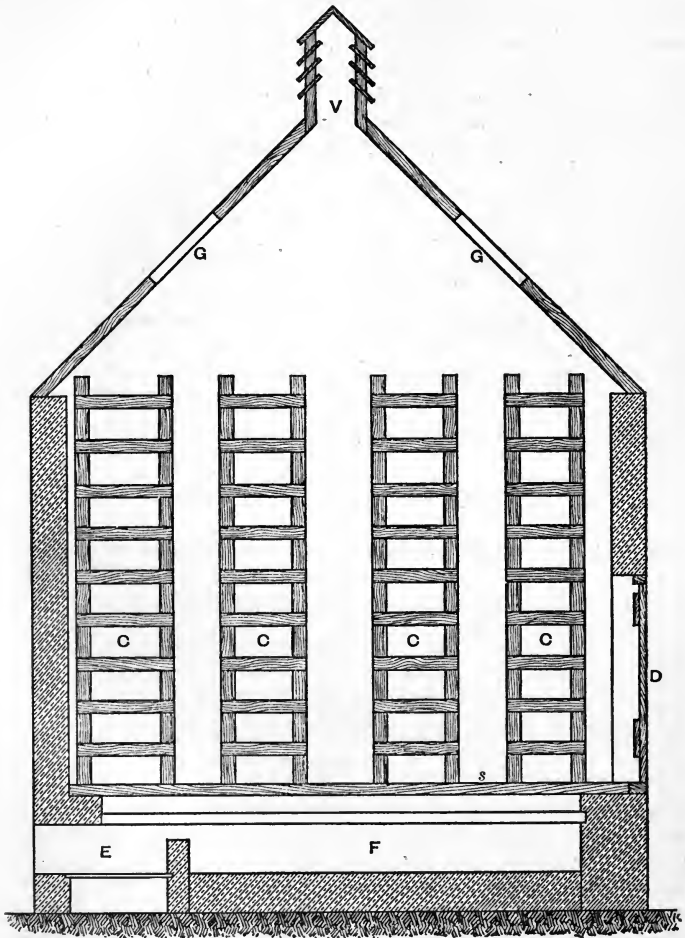


Fig. 29. — Drying stove for pigments.

In dealing with barytes and china clay, special forms of drying stoves have been described.

Some pigments, like the two just mentioned, the oxide reds, burnt umbers, burnt siennas, ultramarine, Guignet's green, are capable of standing a high temperature without being altered in shade; these may be dried in a stove heated to a high temperature, in which case the drying is done quickly. On the other hand, certain colours, such as the chromes, Prussian blue, emerald green, &c., must be dried slowly; for such colours the stove shown in Fig. 30 would be very useful. The two sides not represented in the drawing are of brick, and support the roof.

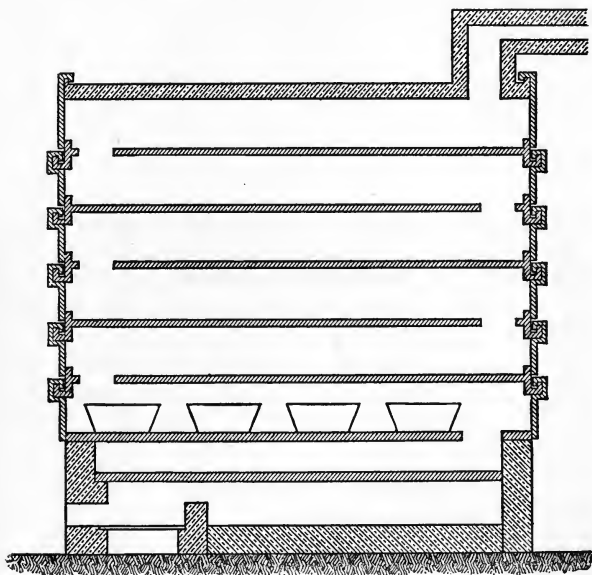


Fig. 30.—Drying stove for pigments.

Stretching from side to side are a number of iron shelves just far enough apart to take an earthenware pan and leave a little space between it and the shelf above. These shelves do not stretch completely from back to front, but, as shown in the drawing, they are arranged to come alternately flush with the front and back, the side of the shelf nearest the front and back of each shelf being turned up to form a flange. The front and back of the stove are made of a number of iron plates, which form a series of doors to the shelves, the top of the plates being bent over to catch on the flange of the shelf above, as shown in the

drawing; it is not necessary that the doors should fit air-tight. A fan at the top of the stove creates a current of air through it, a chamber at the bottom is kept hot by steam pipes, or flue from a furnace; through this chamber passes all the air that is allowed to go into the stove; this hot air passing over and under the colours dries them, and, being hot, absorbs and carries away the water vapour liberated from the wet colours. This stove is effective and economical, and is so constructed that the pans of colour can be readily removed and the shelves quickly refilled.

A drying stove has been constructed in the following manner. A cylindrical vessel was constructed of iron plates of any convenient size. This was divided into three chambers by two perforated iron plates; in the central chamber, which is the largest, is placed the material to be dried; the bottom chamber is kept hot by means of steam pipes, and is provided with an opening to admit air. The upper chamber is fitted with an exhaust fan, so arranged as to draw the air out of the central chamber; the perforations in the plate dividing the central from the top chamber are larger than those in the plate dividing the bottom from the central chamber, the consequence being that the air is drawn away from the central chamber faster than it enters from the bottom hot air chamber, so that a partial vacuum is created in the central chamber which is beneficial to effective drying.

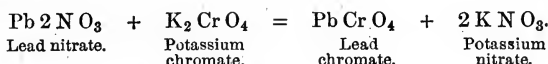
In any stove the colours are best placed in earthenware pans of about 12 to 16 inches in diameter, and 3 to 6 inches in depth; smaller pans may be used, but it is not advisable to exceed the sizes just given. Pans made of galvanised iron have been used, but these are liable to rust and so lead to discolouration of the pigments dried in them; enamelled iron pans, which can now be bought at a reasonable figure, are well worth a trial as being lighter and less liable to break than earthenware pans.

PREPARING PIGMENTS OR COLOURS BY PRECIPITATION.

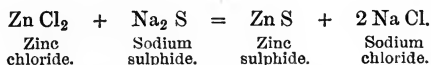
Many colours—the chrome-yellows, Prussian blues, Brunswick greens, lakes, &c.—are prepared by a process of precipitation, the principle of which is that when two or more substances in the state of solution are mixed together a reaction sets in—what the chemist calls double decomposition occurs—and new products are formed; one of these being insoluble in the liquid used is thrown down or precipitated out of the solution, usually in the form of

a fine powder. Thus when to a solution of nitrate of lead, one of chromate of potash is added, a yellow powder falls down; this on examination is found to be chromate of lead, while the liquor contains nitrate of potash in solution; thus there has been an exchange of constituents, the chromic acid has left the potash to form lead chromate, while the potash has combined with the nitric acid of the lead nitrate to form nitrate of potash; the chromate of lead forms a precipitate because it is insoluble in water.

Put into the form of a chemical equation this reaction is expressed as:—



Another example of precipitation met with in colour making is that of zinc sulphide, from solutions of zinc chloride and sodium sulphide, which is represented in the following equation:—

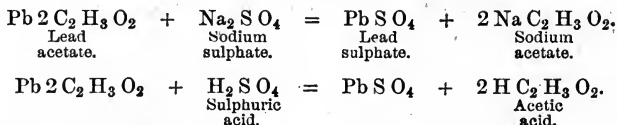


Here, again, there has been an interchange of constituents, and the zinc sulphide being insoluble is thrown down as a precipitate.

As precipitation is a chemical reaction it always takes place in fixed and definite proportions; thus in the preparation of chrome-yellow it is found that 331 parts of lead nitrate interact with 194 parts of potassium chromate, the result being that 323 parts of lead chromate are precipitated while 202 parts of potassium nitrate are left in solution; should the salts be mixed in any other proportion, then one or the other must be in excess, and this excess will be wasted; thus, suppose 150 lbs. of lead nitrate and 95 lbs. of potassium chromate are used; the latter quantity is not sufficient to precipitate all the lead from solution; consequently, the excess, which is 7 lbs., remains, and is practically wasted. The necessity of using equivalent proportions of the materials is a matter of importance as regards economy in making colours by precipitation.

Every case of precipitation is a case of double decomposition, so that the main product is always associated with bye-products, which are sometimes worth recovering, or which may be utilised in other ways. Thus, in making chrome-yellow by the process mentioned above, potassium nitrate in solution is a bye-product;

in places where fuel is cheap it might pay to boil down this solution and recover the salt. Then again, by paying attention to the bye-products, and their probable use in other ways, it is possible to effect economies in the production of colours. Thus, supposing lead sulphate is to be made, this can be done by precipitating a solution of lead acetate, with either sodium sulphate or sulphuric acid, as shown in the following equations:—



In the first case, sodium acetate is formed, and although this has cost money, yet it must be thrown away, because it cannot be economically recovered by the colour-maker. In the second case, the acetic acid formed may be utilised in producing a fresh stock of acetate of lead from metallic lead; in this case there are no waste products, and the manufacture of the lead sulphate is conducted most economically.

The character of the precipitate formed is modified in regard to its tint, its consistence, and in other ways by the conditions under which it is obtained. Thus, if barium sulphate be precipitated from cold solutions, it falls down as a very fine, rather light powder, which is difficult to filter; but if thrown down from hot solutions, it is not so fine, and can be filtered more readily. Again, in making chromes, the conditions under which the operation is performed have a wonderful influence on the result; a difference in the lead salt influences the tint, the nitrate giving a finer product than the acetate. The temperature also modifies the result considerably. Thus, the chrome which falls down from cold solutions is much paler and more voluminous than that obtained from hot solutions. The acid or neutral state of the solution also has some influence, while the presence of such bodies as alum or sulphate of soda has a material influence.

In making colours by precipitation, the following conditions affect the character of the resulting pigment:—(1) Strength of solution. Generally, weak solutions yield finer and more voluminous precipitates than strong ones. (2) Temperature. From cold solutions the product is usually finer and more voluminous than from hot solutions. (3) Proportion between the interchanging bodies. This also has some influence on the result. Thus, in making chromes it is preferable to keep the lead in excess; if a soluble Prussian blue is required, then the potassium

ferrocyanide must be in excess. Other examples might be given illustrative of this point. (4) The order of mixing is important. If the lead salt, in making chromes, were added to the bichromate of potash, the pigment obtained would not be so fine as in adding the bichromate of potash to the lead salt. In making soluble Prussian blue it is important to add the iron salt to the potassium salt, not *vice versa*. In making emerald green, the acetic acid should be added to the copper before adding the arsenic preparation, if a good result is to be obtained. There is another feature in precipitation worth mentioning here. When a solution of a metallic salt is added to another solution containing two other salts, both capable of precipitating the first, it may happen that a kind of selective action may take place; the metallic salt will at first form a precipitate with one of the mixed salts only, and not until this action has ceased will it precipitate the other. An excellent example is the action of silver nitrate on a mixture of sodium chloride and potassium chromate; with the first it will give a white precipitate of silver chloride, with the second a dark red precipitate of silver chromate. When the two salts are mixed together, the silver nitrate will not precipitate the chromate until all the chloride has been thrown down, which point is shown by a change in colour of the precipitate from white to red. Another example is the precipitation of a mixture of sodium chromate and carbonate by zinc sulphate; in this case zinc carbonate is first thrown down. In precipitating a mixture of potassium bichromate and sulphuric acid with lead acetate, lead sulphate is thrown down before the lead chromate. This is a very interesting feature in precipitation, and is often taken advantage of by chemists for the separation of substances, one from the other; they know it as fractional precipitation.

The plant required for making colours by precipitation is comparatively simple. There are required, 1st, vessels wherein to dissolve the various ingredients used; and 2nd, vessels in which the ingredients are mixed together, precipitation vessels, which are preferably of wood, as those of earthenware would be too easily broken, and could not be made so large as required. The two classes of tanks or tubs should be kept distinct; a dissolving tub should not be used for precipitating in. Then each colour that is made should have its own set of tubs. If a set of tubs were first used for making a chrome-yellow, and then for making a Prussian blue, the results in the second case would not be very satisfactory; the rule of a colour shop should be that every distinct colour has its own set of tubs. The reason

for such a course is that it is practically impossible to clean the tubs so as to avoid the liability of the remnants of one batch spoiling the next batch.

Fig. 31 shows a good arrangement of plant for preparing pigments by precipitation; a set of five tubs is shown; two of these, CC, are placed on the floor, and used for the actual precipitation; three, DDD, used for making solutions of the ingredients, and which may be smaller than C, are placed on a platform, P, above C. A steam pipe, S, with branch pipes, carry steam to all the tubs for the purpose of heating the contents, if that be necessary;

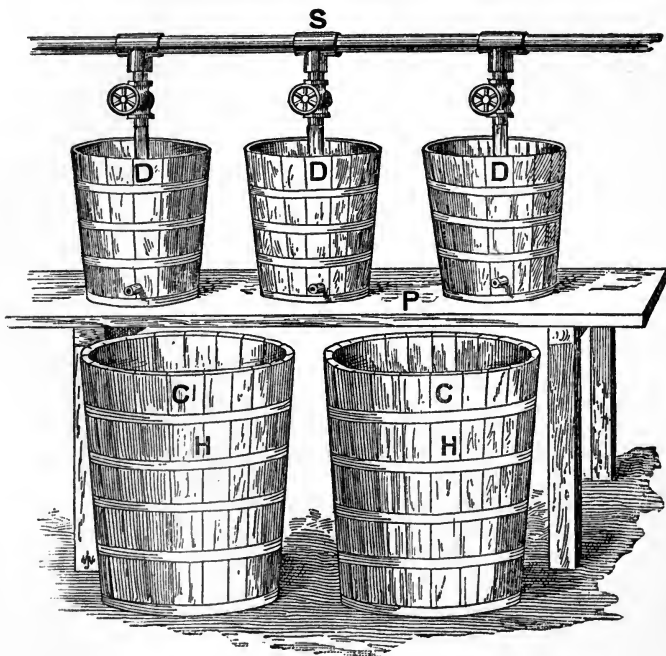


Fig. 31.—Plant for preparing pigments by precipitation.

arrangements may be made for conveying water to these tubs. In the bottom of the tubs are plug holes or tap holes, which allow of the contents, when ready, flowing into C, through troughs. C has a number of holes, *h, h, h*, fitted with plugs, by the removal of which the supernatant liquors are easily

run off after the pigment has settled. Or the liquors may be siphoned off. Although a set of five are shown in the drawing as being an economical number, yet three only are, as a rule, required to be used at one time for preparing a pigment, but with five two batches of a pigment requiring the same materials may be more readily prepared. The size of these tubs must be proportioned to that of the quantity of pigment required to be turned out. A convenient size for the dissolving-tubs is 3 ft. 6 in. high, by 2 ft. 6 in. diameter; the capacity being about 110 gallons; the precipitating tub may be 3 ft. 6 in. high by 3 ft. 6 in. diameter, and will hold 320 gallons; batches of 7 to 10 cwts. of colour can easily be made in such tubs.

The usual method of procedure in making pigments by precipitation is as follows. The materials, after being weighed out, are placed in the dissolving-tubs with the requisite quantity of water; then, by means of the steam pipes, they are heated until complete solution has been effected. The liquors are now run into the precipitation tank, if they are to be used hot, or they may be allowed to cool before running into the precipitation tub. While running into the tub, it is desirable that the liquors be thoroughly mixed by stirring together. When all the liquors have been run into the precipitating tub, the mass is allowed to stand for the precipitate to settle; when this has occurred, the clear liquor is run off, fresh clean water run in, the precipitate stirred up and again allowed to settle out, and the water run off; if necessary, this washing is repeated once or twice; finally, the precipitate is allowed to settle, the clear top water run off as much as possible, the precipitate thrown on to a filter for the rest of the water to drain away, and the still wet precipitate placed in the drying stove to dry.

In making some pigments, such as rose pink, the lake-pigments from the coal-tar colours, vermilionettes, &c., solid bodies such as barytes, whiting and orange-lead are added. This is best done by running one of the solutions into the precipitating tub, adding the barytes, &c., and stirring so as to get every particle of the solid thoroughly incorporated with the liquor; then the other solution is run in and the operation finished as described above. Unless care is taken to ensure the thorough mixing of the dry solid added with the liquors, the resulting pigment will have a speckled appearance.

In preparing pigments from such natural materials as log-wood, cochineal, fustic, Brazil wood, &c., where the whole of the material is not dissolved, the actual colouring principle should be extracted by boiling in an apparatus so constructed as to permit

the colouring principle being extracted and removed by boiling from the insoluble particles of wood, &c. Further details are unnecessary, as the extractors made are numerous and efficient. A simple form would be a boiler fitted with a perforated false bottom, on which the dyewoods, &c., are thrown; a similar perforated plate is placed on the top of the mass, and the whole boiled with water; when the extraction is considered to be finished, the liquor is run off below the false bottom, and through a filter into storage tanks, in which it is kept until required for use.

FILTERING.

Filtering, which follows precipitation, effects the separation of the pigment from the excess of water it contains. The simplest plan is to use a filter constructed of a sheet of calico loosely stretched over a skeleton framework of wood (see Fig. 32). The wet pigment from the precipitating tanks is thrown on to this sheet of felt; the water drains through, while the pigment remains on the top of the sheet.

On the whole, the process is an effectual one, and the filtration

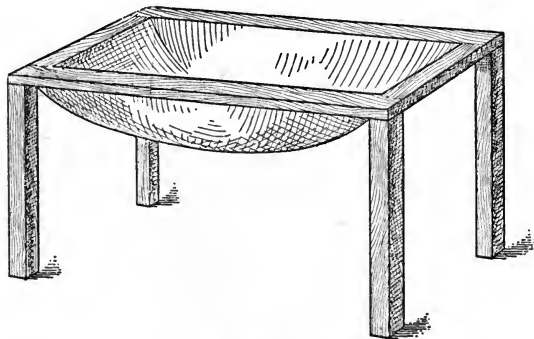


Fig. 32.—Filter.

is thorough; the speed and completeness depends upon the character of the precipitate and the quality of the filtering cloth. If the precipitate is powdery and somewhat granular in structure, then the filtering goes on fairly rapidly, and the liquor that drains away is fairly clear. On the other hand, there are precipitates, such as Prussian blue and blanc fixe, that are very fine, rather slow in filtering, and from which it is difficult to obtain a clear liquor.

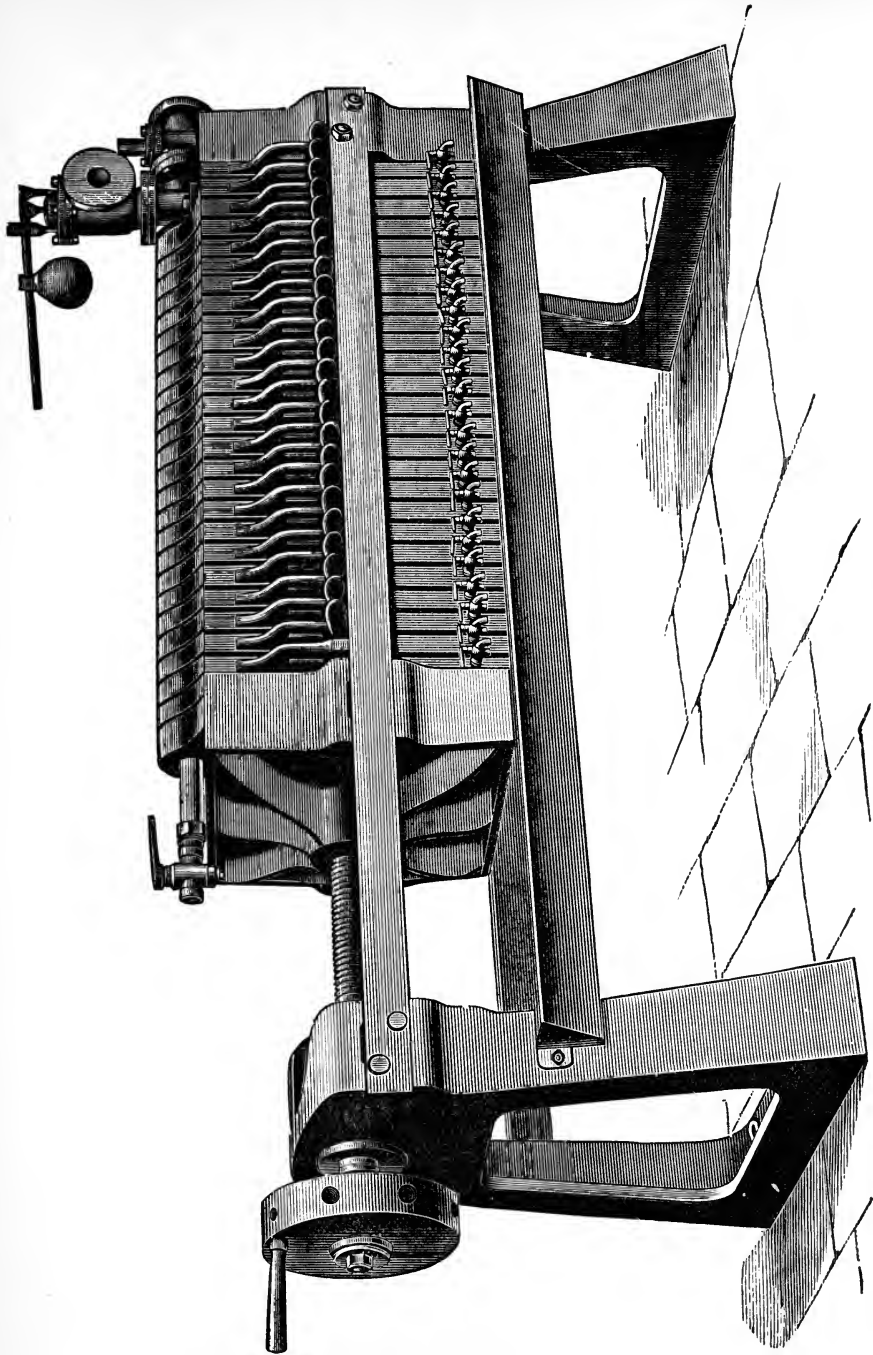


Fig. 33.—Filter press.

The character of the filter cloth should be adjusted whenever possible to that of the pigment to be filtered; if of open texture it will filter rapidly, but for fine precipitates such as blanc fixe, Prussian blue, chrome-yellows, &c., it is not suitable; it can be used for coarse precipitates, like oxide of iron, Derby-red, lakes, &c. Fine filter cloths filter slowly, but the filtration is thorough; such cloths must necessarily be used for the fine pigments named above.

The modern filter press, such as shown in Fig. 33, has not yet been generally adopted in colour shops, although its use would greatly facilitate the filtration of pigments. Its cost may exclude it from small colour works, but in large works, where quantities of pigments are turned out, its use will be found to save both time and labour.

It consists essentially of a number of flat chambers, formed of iron frames covered with filtering felt, placed side by side on a suitable iron frame and pressed against one another by means of a screw or hydraulic press. The material to be filtered is pumped into the chambers, the liquor flows through the felt, while the pigment or solid matter is retained within the chamber. When it is considered that enough has been sent through the filter press, it is taken apart, the cakes of pigment removed from the chambers, and sent forward to the drying stove.

The efficiency of these filter presses depends upon the workmanship given to the machine by the makers; every part must fit well, otherwise the filtration is imperfect. The quality of the filter cloths also has some influence. Generally, these presses require finer cloths than the simple filter described above, and, of course, fine precipitates will require finer filter cloths than coarse precipitates. These points can only be alluded to here in a general way; each colour maker must find out what quality of filter cloth will best suit the press he is using and the pigment he is filtering; and in a similar way, the best conditions of pumping and the pressure used must be found out.

Another method of filtering is by the vacuum filter press, one form of which is shown in Fig. 34. This consists of a hemispherical vessel of copper divided into two parts by a perforated plate. The top part is open; the bottom part is closed; but has two openings, one of which serves as the outlet for the liquor which runs into the lower part, while the other is connected with a vacuum pump. The mode of using is comparatively simple. The perforated plate is covered over with a sheet of filter cloth, the material to be filtered is thrown on to it and the vacuum pump set at work; the liquor runs through, leaving the

solid matter on the top of the filter. This method of working is very simple and efficient, quicker than the first method described, but not so quick as the filter press. Other forms of these vacuum filters have been made. One form consists of a conical vessel fitted on the top of a strong iron box; between the two is a per-

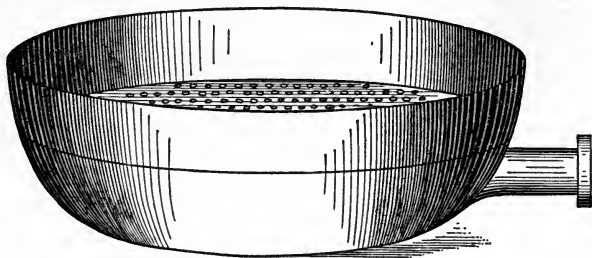


Fig. 34.—Vacuum filter.

forated plate or a sheet of wire gauze, on the top of which is placed a sheet of filter cloth; the material to be filtered is thrown into the cone, the air in the iron box is pumped out by a vacuum pump, the liquor is forced or rather pulled through, leaving the solid matter in the conical vessel.

GRINDING.

To fully develop the beauty of a pigment, and make it best adapted for conversion into paint, it is necessary to grind the materials very fine. Formerly this was done by hand on a slab of marble, with a muller. This is necessarily a slow and tedious process, only applicable to turning out small quantities of pigment or paint, and which is not admissible where large quantities are required, as in these days of ready-mixed paints. Grinding mills are, therefore, a necessary part of the plant of a modern colour-works.

Grinding is peculiarly a mechanical operation, it is rarely that chemical action plays any part in it; the only examples are, perhaps, oxalate of iron yellow, Naples yellow, and mercury iodide scarlet, which are affected by iron and must be ground in stone mills. These pigments are only used by artists, and in small quantities. As a rule, the manufacturer of house paints need not trouble himself as to the material his mills are made of

so long as they are efficient, although those with granite or stone grinding surfaces are to be preferred to those which have them of iron, as being least likely to affect the tints of the pigments ground in them.

The grinding mills in use are constructed on one of three principles, and, therefore, may be divided into three groups:—

1st. Edge-runner mills.

2nd. Flat-stone mills.

3rd. Roller mills.

The first two kinds have been used for grinding purposes for centuries, so that nothing is known as to who invented them, or as to where they were first produced. Probably they were at first very simple in construction, and were afterwards modified so as to increase their grinding efficiency. The third group is of modern invention, having been introduced during the last forty years; but even the name of its inventor is not definitely known.

1st. **Edge-runner Mills.**—This form of grinding mill has been in use for centuries for grinding corn, stones, and other materials. The essential principle of these mills is that of a circular stone or runner, set edgeways, and running in a circular basin-shaped trough or hopper and bed, on which the material to be ground is placed, and the stone rolling over it crushes it to powder. Many forms of this edge-runner mill are made, and it is also made in a great variety of sizes, suitable for the various materials usually ground in such mills. In some forms the trough and bed is made to revolve, while the runners are made to turn on fixed centres or axes by the friction of the bed on their edges; in other forms the bed is fixed, and the runners rotate on a movable central shaft. In this case the runner has two motions—one on its own axis, by friction with the bed, and another round the axis of the bed. In some mills the driving motion is applied from above, in others from below. Besides the arrangements for driving the runners, there is also a number of scrapers provided to keep the edge of the runners from becoming covered with a cake of the ground colour; other scrapers are fitted to the bed of the mill to keep the material under the runners, and prevent it from getting into the corners, where it would not be ground. Usually, also, the central shaft is provided with springs, so that should an exceptionally hard piece of material pass under the runners the latter will tilt a little, and allow the piece to pass without doing any damage.

Fig. 35 is a drawing of an edge-runner mill, such as is specially used for colour grinding. This is made in several sizes, but a

useful size is one having stones about 3 feet in diameter, and 10 to 12 inches thick. Such a mill is capable of grinding from 1 to $1\frac{1}{2}$ tons of colour per day, but the quantity will necessarily vary with the character of the material which is being ground. Some natural oxides are rather hard, and 1 ton may be taken as a fair day's work; on the other hand, soft ochres may be ground at the rate of 2 tons a day. Much, too, depends upon the degree of fineness of the grinding; the finer it is the smaller will be the quantity turned out.

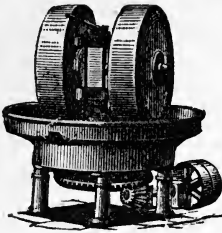


Fig. 35.—Edge-runner mill.

In Fig. 36 is shown a section of Messrs. Follows & Bate's newest form of edge-runner mill. In this the bed is made of granite, 4 feet 8 inches in outside diameter; the runners are also made of granite, and are 30 inches in diameter and 8 inches wide. The hopper is made of hard wood, the bearings of the

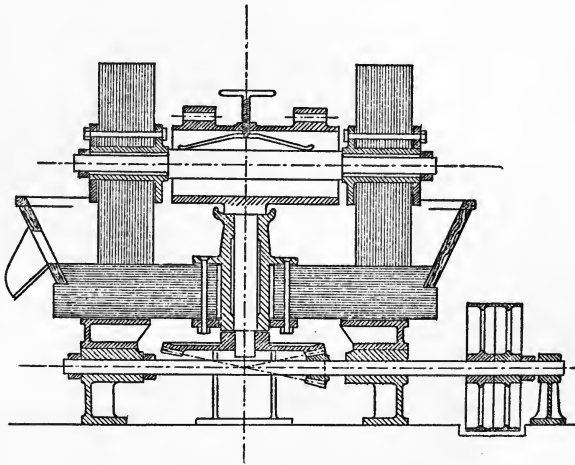


Fig. 36.—Edge-runner mill.

runners of lignum vitæ, and scrapers (not shown in the section) also of the same hard material; thus the pigment or other material being ground does not come in contact with any metal; therefore, it is not liable to be deleteriously affected. Further, the mill can be kept cleaner than is possible with a metal hopper

and bed, especially where the mill is only occasionally used. The mill is under-driven.

In some respects under-driven edge runners are not so stable as over-driven mills, owing to the necessity of raising them above the floor level; on the other hand, small mills are more convenient to work with when driven, while for heavy grinding and large sizes of mills those which are over-driven present some advantages. Where in addition to a grinding action there must also be a mixing action, the edge runner mills will be found to possess some points of advantage over flat stone or roller mills.

Edge-runner mills are very useful for the first coarse grinding of hard material, and for such natural pigments as the oxides, ochres, umbers, barytes, gypsum, &c. They cannot compete with the flat-stone or roller mills for fine grinding.

2nd. **Flat-Stone Grinding Mills.**—Grinding mills con-

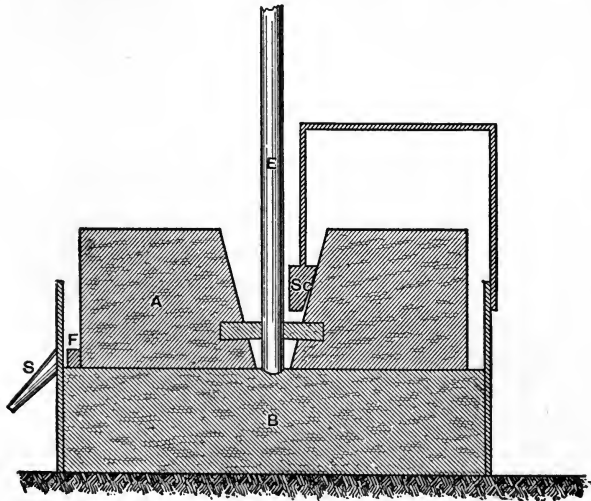


Fig. 37.—Flat-stone grinding mill.

structed on the principle now to be mentioned have been known for a very long time, and have been made in several forms for grinding all kinds of materials. As a rule, they are very efficient. In these flat-stone mills there are two grinding surfaces of a circular form, not necessarily (although usually) horizontal; one of these (usually the lower one) is fixed, while the other is made

to rotate on the top of the fixed surface ; the material to be ground is usually fed between the two surfaces at the centre, and the motion of the mill is such as to cause it to pass outwards to the edge ; in doing so it becomes ground.

Fig. 37 represents a simple form. A is the top stone, which is usually about 1 foot thick and 2 feet in diameter. In the centre is fitted the driving shaft, E; the centre of the stone is hollowed out in a conical shape, forming a hopper, down which is fed the material to be ground; usually a scraper, Sc, scrapes the material from the sides of the hopper, and causes it to pass down to the bottom. The fixed stone is represented at B, and is often a fraction larger than the revolving stone; the ground material oozes out at the edge between the two surfaces, and is collected by a scraper, F, and passed down the shoot, S, into a receptacle for it placed below. Often a number of these mills are placed side by side on a bench, a shaft overhead supplying the necessary driving power; by suitable clutch-gearing the mills can be thrown into and out of gear as may be required.

The quantity of material ground in such mills varies considerably, and is dependent on the kind of material and the degree of fineness of the grinding; usually from $\frac{1}{2}$ to 1 ton of material may be considered a fair day's work.

The surfaces of the stones are usually corrugated so as to increase the cutting or grinding power of the stones; these corrugations are arranged rather differently by various makers of these mills; in some they radiate entirely from the centre, in others some radiate from the centre and some are more or less

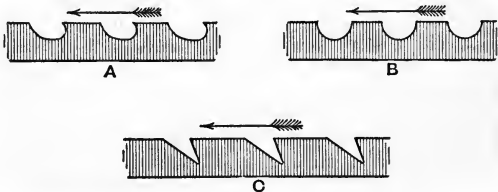


Fig. 38.

tangential to the circumference. Their shape has some influence on the grinding power of the stone mill; the best form is that shown at A in Fig. 38, the stone moving in the direction of the arrow; the back edge of the corrugation acts like a pair of shears on the material, and cuts it; the shape shown at B is bad, as such a stone has little grinding power. C is a shape commonly met with in mills with metal grinding surfaces.

For paste colours, it usually suffices to build a small trough round the edges of the stones, which serves to collect the ground colour as it oozes through from between the stones.

Some makes of these flat-stone mills have the grinding surfaces constructed of hardened steel; or one surface of granite, the other

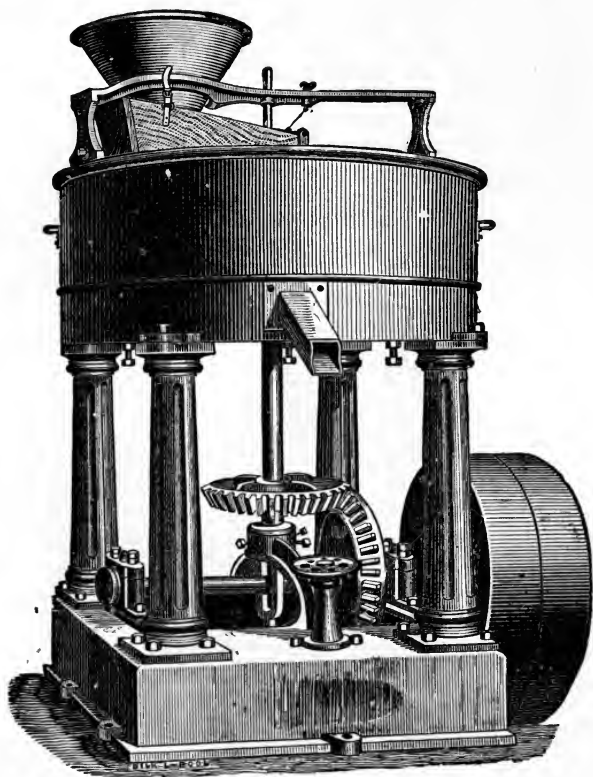


Fig. 39.—Levigating grinding mill.

of steel; or both grinding surfaces of granite. Modern makes drive the moving stone from underneath, in which case the top stone is a fixture, while the bottom is made to revolve. A variety of such a mill is shown in Fig. 39; Messrs. Rushton & Irving's levigating grinding mill, which shows very well the general form of such mills. When used to grind crude earthy

pigments, like ochres, siennas, umbers, &c., which are to be subjected to levigation, these mills are (like the one shown) cased in, the water and crude material is sent in by the hopper on the top of the mill, while the water and ground material flows out through the spout below into the necessary settling tubs.

To such mills screws are adapted to regulate the pressure between the grinding surfaces, and, therefore, the degree of fineness to which the materials are ground; the greater the pressure, the finer the material; on the other hand, the amount of material which can be ground in a given time is materially reduced. These flat-stone mills are usually very efficient, and some paint grinders prefer them to other forms. Certainly they, as a rule, take up less floor space than edge runners or roller mills, and a number can be readily and conveniently arranged on a stout bench along the wall of the grinding shop.

Cone Mills.—Another form of mills constructed on the prin-

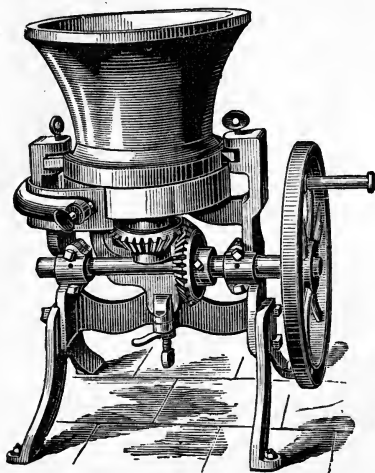


Fig. 40.—Cone paint grinding mill.

ciple stated above is that known as the cone paint mills, shown in Fig. 40, which is a drawing of one of Messrs. Follows & Bate's cone mills. These mills are always driven from underneath. Fig. 41 is the same mill shown in section, whereby the construction of the mill can be better seen. The top grinding-surface is formed by the bottom edge of a fixed hopper,

into which the material to be ground is fed. The bottom grinding-surface is made of a conical shape, and fits closely against the edge of the hopper. The actual grinding surfaces are portions only of the hopper and the cone respectively, and these portions are usually corrugated so as to increase the grinding action, the corrugations starting from the centre and tapering towards the outer edges, to which, however, they do not extend. A screw arrangement under the mill serves to regulate the distance apart of the two surfaces, and consequently the fineness of grinding. The material is fed into the hopper, a revolving knife in which serves to keep the materials well mixed together;

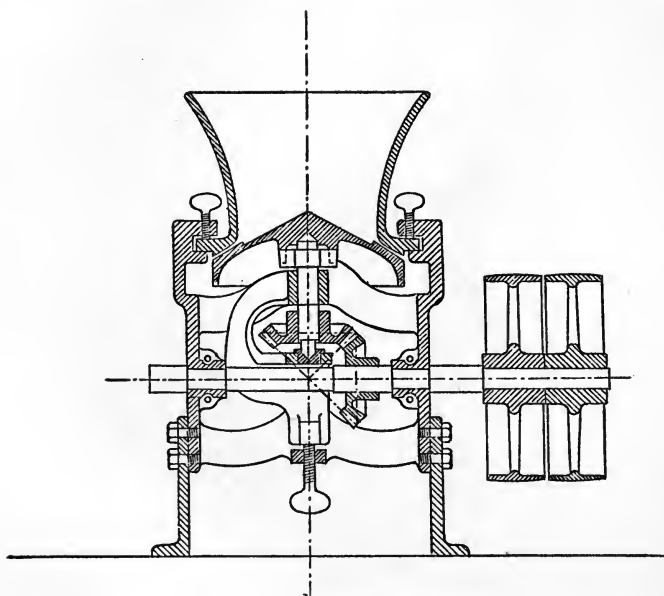


Fig. 41.—Cone paint grinding mill.

the ground material passes out from between the surfaces, and is scraped off by a suitable scraper; in modern forms of this mill a trough is provided for the ground material to collect in; this trough can be emptied from time to time as may be required.

These cone mills are made in various sizes, from mills small enough to be driven by hand (Fig. 40) to those large enough to require power (Fig. 41). They are serviceable for all kinds of

materials, and particularly for wet paints. By being fitted with covers and covered spouts, they may be used for grinding enamel paints, varnish paints, and other like materials containing volatile liquids.

The quantity of material these mills are capable of grinding varies with their size, but a mill having grinding surfaces 12 inches in diameter will grind from 12 to 15 cwts. per day; but these mills can be had for grinding any quantity up to 40 cwts. per day.

In Fig. 42 is shown a sectional view of Messrs. Follows & Bate's latest form of cone mill, which they call a disintegrator.

This mill is adapted for grinding friable materials which are offered to the mill in comparatively large pieces. It will be seen that the grinding surfaces are very deeply serrated, especially where the material first comes in contact with them, while the extreme edges are not serrated, so that the materials are ground very finely. The machine is strongly built, takes but a small power to drive, and does its work well; every part is easily accessible for cleaning, while a cover prevents any of the material from flying about. This mill is best suited for grinding dry materials, not for paste or wet colours.

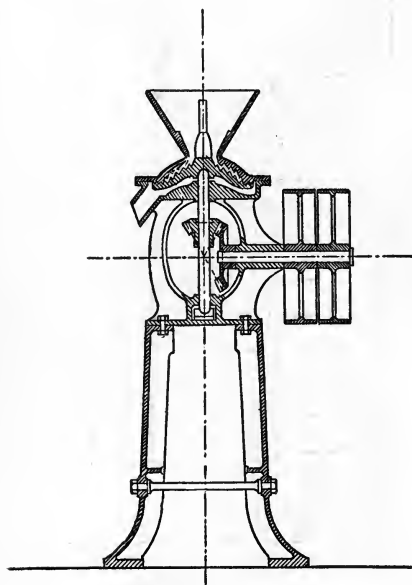


Fig. 42.—Cone grinding mill.

Messrs. Rushton, Irving & Co., of Liverpool, made an horizontal cone mill (shown in Fig. 43), in which the grinding surfaces are arranged vertically. Unlike other cone mills, the grinding surfaces are, in this mill, made of French burr stone, the fixed surface being made concave, while the revolving stone is made convex and ground, after being fixed on its spindle, to

fit the concave surface. Both surfaces are furrowed to suit any special work for which they may be required. By means of a screw the pressure between the surfaces, and, therefore, the

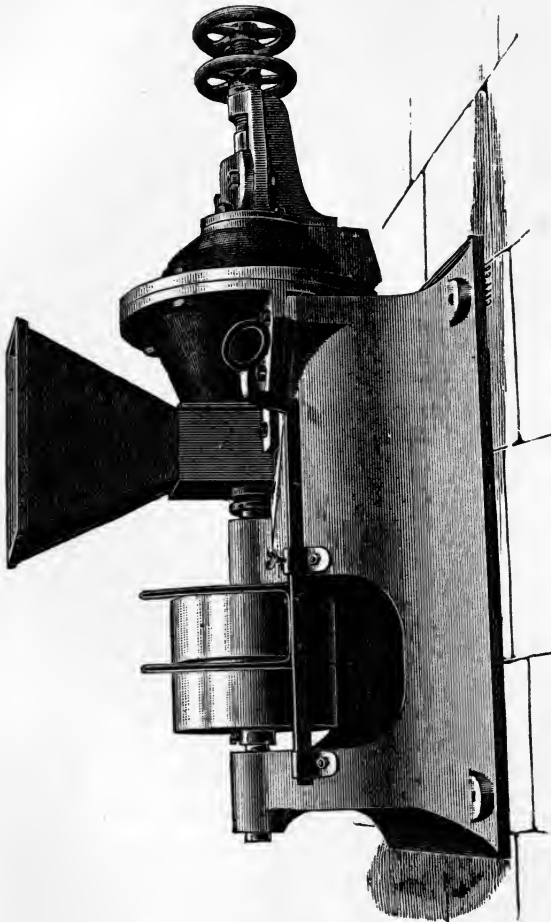


Fig. 43.—Horizontal cone grinding mill.

degree of fineness of grinding, can be regulated. This mill does its work well, takes up comparatively little floor space, and, for

quality of work done, is much better than the edge runner mills. Owing to being placed direct on the floor and low in construction, they are remarkably steady in running, and are convenient for feeding the rough material.

3rd. **Roller Grinding Mills.**—Roller grinding mills are only of comparatively modern introduction, but they are now in very extensive use for grinding all kinds of materials, and have dis-

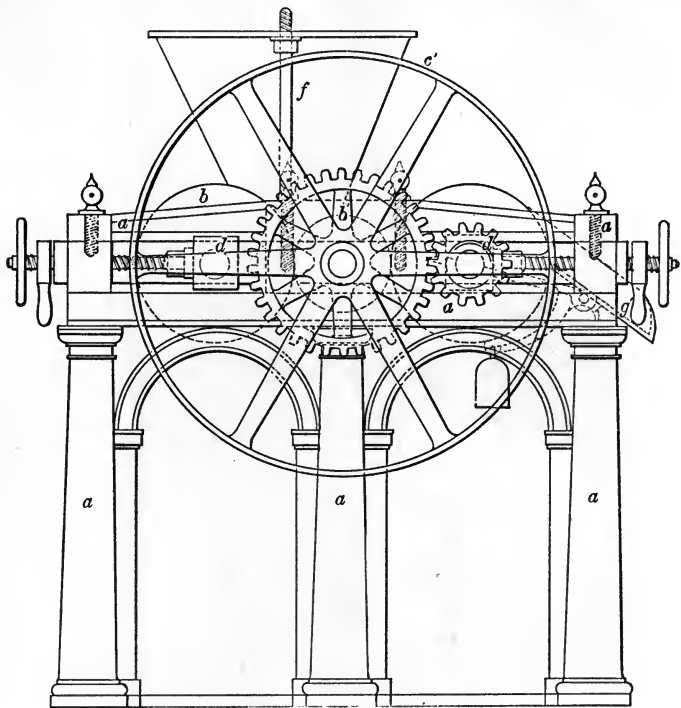


Fig. 44.—Geyelin's roller grinding mill.

placed the flat-stone mills to a very considerable extent. The first roller mill which was invented was patented in 1852 by an engineer named *Jack*, and consisted of a roller working in a curved horizontal surface, a form which presented many disadvantages, and probably never came into extensive use.

The form which the roller mill takes to-day was first patented in 1852 by *J. K. Geyelin*, whose mill is shown in Fig. 44. These

mills are, however, generally known as *Clark's* roller mills, from the name of the first maker, Mr. B. H. Clark. Geyelin's mill had three rollers horizontally placed in a suitable framing; the rollers could be either conical or cylindrical; the middle roller was the driving roller, and was connected with the other two by spur wheels arranged in such a manner that the speeds of revolution of the three rollers were different.

Screws for regulating the pressure between the rollers are provided, as also tension springs between the bearings, to allow a little play between the rollers in case any hard material should happen to accidentally get between them. A hopper between the first two rollers serves for the introduction of the material to be ground, while a scraper takes off the ground material from the last roller. Geyelin's mill includes many points of detail more fully worked out in the more modern forms of these roller mills.

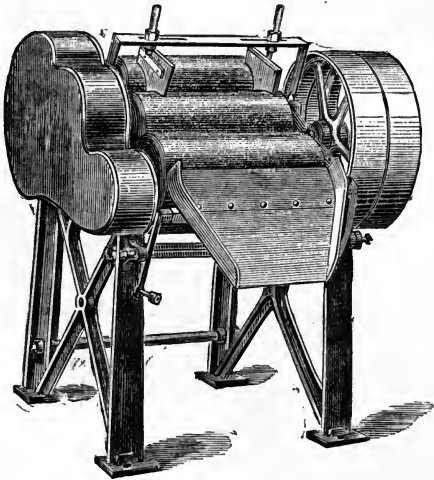


Fig. 45.—Roller grinding mill.

Fig. 45 shows a roller mill made by Messrs. Ritchie & Co., which has the three rollers arranged in an inclined plane, which it is obvious must be an improvement on the horizontal arrangement. A convenient size of such a mill has rollers measuring 22×14 inches, the middle roller working at a speed of 55 revolutions per minute, the other rollers at different speeds; it is

capable of grinding from 3 to 4 tons of ordinary colours, or 8 tons of white lead, in a working day of 10 hours.

Fig. 46 is a drawing in section of Messrs. Follows & Bate's three-roller mill, with rollers 24×12 inches; all are driven from

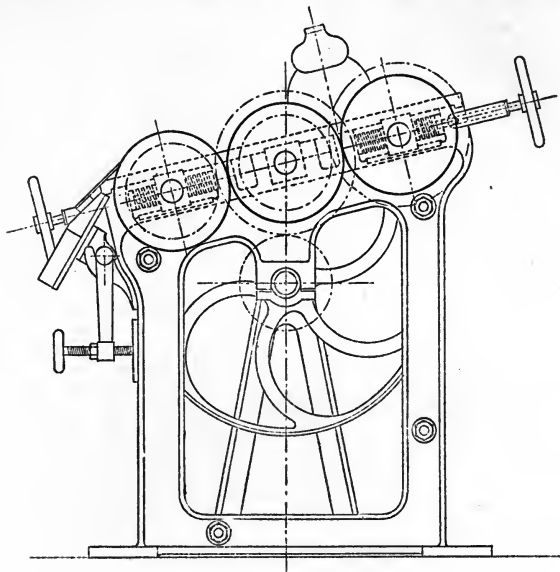


Fig. 46.—Roller grinding mill.

the central one with spur gearing, so that they revolve at different speeds, the feed roller at 40, the middle roller at 80, and the delivery roller at 120 revolutions per minute; this difference of speeds much increases the efficiency of the grinding, and ensures that the action of the mill shall be a grinding action, and not simply a crushing action, as would be the case if the rollers all revolved at the same speed. The central roller has a lateral motion imparted to it, whereby a further grinding effect takes place, and there is less risk of the rollers being worn into grooves, which would reduce their efficiency very much. Springs are placed in connection with the bearings, and by suitably-arranged screws the pressure of rollers on one another can be adjusted with nicety. A delivery scraper is provided, as also adjusting guides to regulate the amount of material supplied to the feed rollers.

Fig. 47 shows the combination of the same grinding mill with two pug mills of the construction shown in Fig. 50. One pug mill only is shown in the drawing, but two are usually provided with each mill. These are connected to the main driving shaft of the mill by chain gearing, so that a positive drive is obtained, and there is no slip or loss of power, as would be the case with a belt drive, and there is less noise than if a wheel gearing was adopted; by suitably arranged clutches the pugs may be thrown in or out of gear as may be required. The con-

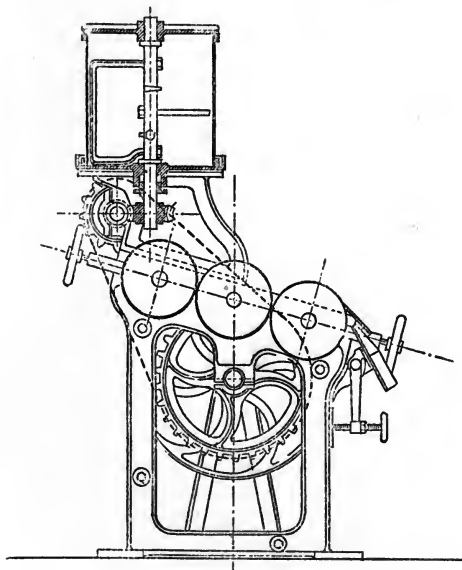


Fig. 47.—Combined roller and pug mill.

tents of the pug mills are discharged on to the roller mill through sluices at the bottom.

In Fig. 48 is shown a very powerful roller grinding mill made by Messrs. Follows & Bate. This drawing will also give a good idea of the general appearance of the roller mill and combined roller and pug mill. Figs. 46 and 47 show it in section only. The large mill really consists of two three-roller mills placed one above the other, so that the ground material from the uppermost mill, which gives the first grinding, passes direct to the lower mill, where it receives a second grinding. A pair of pug

mills is placed above the mills for mixing the materials together which are to be afterwards ground in the mills. The top mill and the pug mills are driven from the driving shaft by chain gear as shown in the drawing.

In Fig. 49 is shown the form of roller mill as made by Messrs.

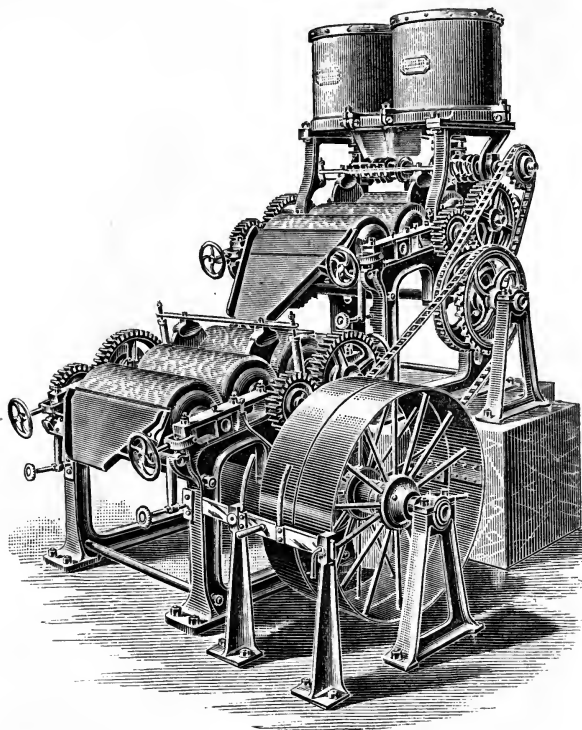


Fig. 48.—Combined double roller and pug mill.

Brinjes & Goodwin. In this mill the rollers, three in number, are placed vertically above one another, two directly one above another, the third slightly on one side of the central line of the other two. The three rollers are not of equal size; the two top rollers are about 10 to 12 inches in diameter, while the bottom roller is from 14 to 16 inches in diameter; they revolve at different speeds, the top or feed roller at 12 revolutions, the

middle roller at 46 revolutions, and the bottom roller at 110 revolutions per minute; this causes a considerable increase in the grinding power of the mill. Hand-screws serve to regulate the pressure between the rollers, while springs between the bearings enable the rollers to give when any hard material gets between them. The middle roller also has a small lateral motion in order to prevent the rollers from being grooved, and to increase

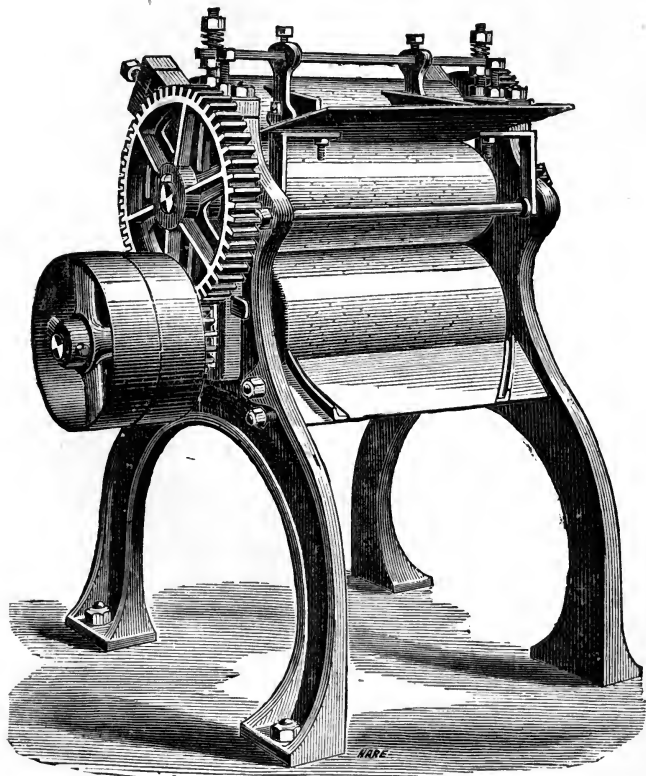


Fig. 49.—Three roller grinding mill.

the grinding action. Scrapers are attached to each roller of this mill to keep the rollers clean and to ensure all material passing between the rollers. A delivery scraper is attached to the last

roller to take off the ground material and deliver it into a suitable receptacle. This mill will turn out from 75 to 100 cwts. of material per day, ground very fine; it is an efficient mill, and invariably does its work in a satisfactory manner, while for very thin paint it is better than other forms of roller mills.

In more recent makes of these mills the tendency is to increase the number of rollers; for very fine grinding it is necessary to run the material twice through the mill to ensure it being properly ground; this repetition increases the labour attached to the process. To avoid this some makers have double mills with six rollers (see Fig. 48) in which the material is ground by the first three rollers and is then passed on to be re-ground by the second three rollers. Other makers arrange four or five rollers in one mill, so that an increased amount of grinding takes place; such mills are apt to get cumbrous and rather difficult to keep clean.

Roller mills are only suitable for grinding colours mixed with oil; they cannot be used for dry colours at all. The principle on which most of them work is that the colour, previously mixed with oil, is fed between the first and second rollers, where it gets a first grinding and, then, adhering to the middle roller, it is carried round, and again ground between the middle and the last roller; then, passing round the third roller it is scraped off by the delivery scraper and delivered into a receiver. The delivery scrapers are, in all the best makes of these mills, kept in contact with the third roller by balance weights which, on the whole, work better than if the pressure of the scraper on the roller was brought about by a wheel and screw arrangement. It is obvious that as the colour is in most forms carried between the second and third rollers by its power of adhesion to the second roller, that dry colours, having little or no such adhesive power, cannot be ground in these roller mills.

Although a roller mill is capable of grinding a large quantity of material in a given time, it is generally considered that they do not grind colours so fine as does a well-built flat-stone mill.

MIXING.

An important part of the plant of a colour and paint shop is the mixing or, as they are often called, the pug mills, in which the dry colour is mixed with the oil, either to form the stiff paste in which so much of the painter's pigments is now sold, or to mix the pigment, oil, &c., into paint ready for use.

The usual form of these pug mills is shown in Fig. 50, which represents one of Messrs. Follows & Bate's pug mills. It consists of a cylindrical casing 20 inches in diameter and 20

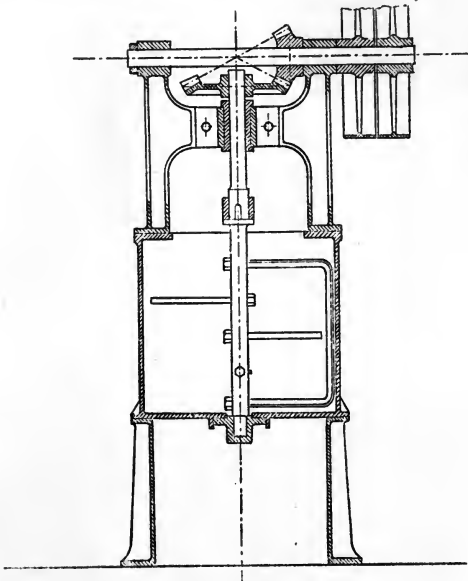
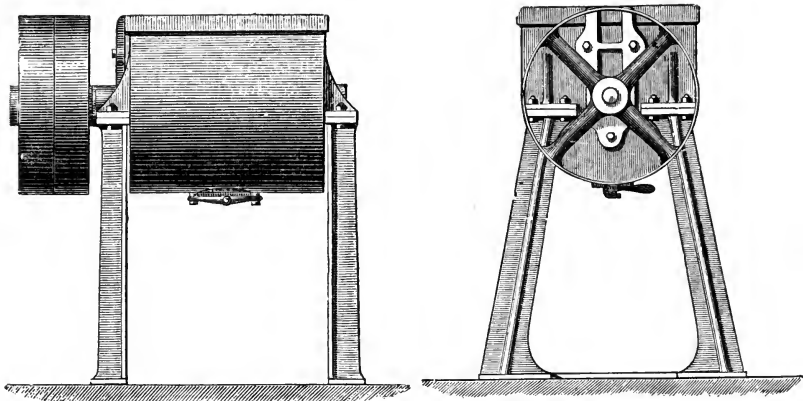


Fig. 50.—Pug or mixing mill.

inches high; in the centre is a revolving shaft carrying arms which effectually mix the various ingredients together; such a pug mill will mix 2 tons of white lead in an ordinary working day. It is customary to arrange a pair of these pug mills in connection with a roller grinding mill, as shown in Figs. 47 and 48, in which case arrangements are made for driving the pugs separately from the grinding mill, so that either one or both may be mixing at the same time, or one be mixing and the other delivering its contents to the grinding mill through the openings in the bottom of the pug mill provided for that purpose.

Messrs. Brinjes & Goodwin place the pugs, as also the stirrers or mixers, horizontally (see Figs. 51 and 52); the stirrers are of a form specially adapted for ensuring a thorough admixture of the various ingredients. They also arrange a pair of these to work in conjunction with their roller mill.



Figs. 51 and 52. — Pug or mixing mill.

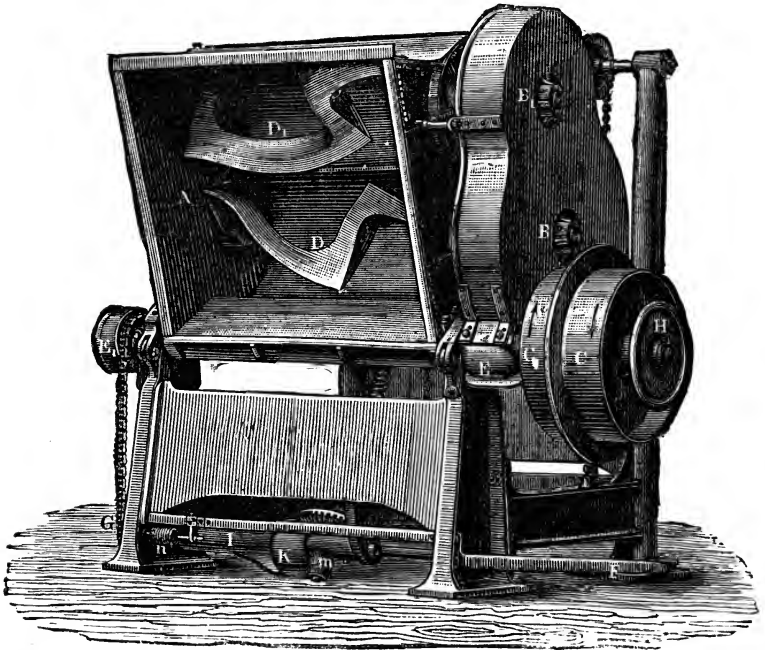


Fig. 53. — Mixing mill.

Fig. 53 represents one of Messrs. Werner & Pfeiderer's universal mixing mills. In it the trough containing the material to be mixed is placed horizontally; there are two mixing blades of a peculiar form, which revolve in opposite directions, one within the other, so as to cause a thorough mixing of the materials. This peculiar construction of the mixing blades is shown in the illustration, which also represents the mill as being tilted for emptying; the working position is with the trough horizontal. These mills are made in a great variety of sizes and forms, and are very effective, doing their work well and thoroughly; they can be used either for dry or paste colours.

A mixing mill of another pattern made by Messrs. Follows & Bate is shown in Fig. 54. This form is very good for mixing

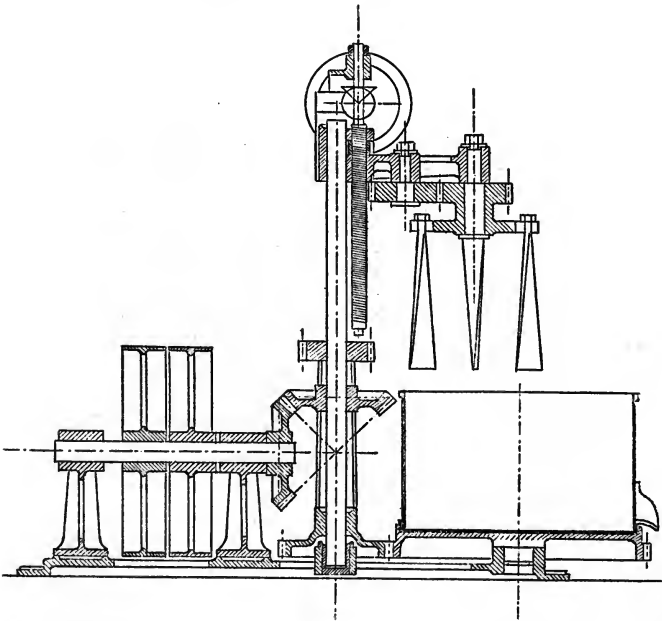


Fig. 54.—Mixing mill.

paint or dry colours together. The materials to be mixed are placed in a can or vessel, and this in turn is placed on an horizontal spur wheel whereby it is caused to revolve. A bunch of

stirring rods is made to revolve by suitable gearing so as to mix the materials in the vessel. Arrangements are provided by means of which the stirrers can be lifted in or out of the vessel as may be required. This mill is an effective one, and capable of getting through a large amount of work.

It is a good plan in mixing oil with the dry colour to pour the oil over the colour at least 24 hours before mixing and grinding, as the gradual absorption of the oil by the colour promotes and quickens their intimate mixture in the pug mill.

The quantity of oil required to grind colours into the stiff paste in which they are now so largely sold varies very considerably with different pigments; some only require a comparatively small quantity of oil, others a relatively large quantity. Even with different samples of the same colour the proportion will vary a little. Different colour makers, too, use different proportions of oil and dry colour in grinding. The following table will give some idea of the proportions usually adopted, which are essentially the same both for raw and for boiled linseed oil:—

White lead,	7½	per cent. of oil.
Zinc white,	22	” ”
Barytes,	7	” ”
Putty,	18	” ”
Black,	27	” ”
Brunswick green,	11	” ”
Red oxides,	10	” ”
Brunswick blue,	11	” ”
Oxford ochre,	16½	” ”
Burnt Turkey umber,	29	” ”
English umber,	20	” ”
Vandyke brown,	40	” ”
Siennas,	37½	” ”
Black in turps.,	55	” turpentine.

These figures are based on practical working, but, as mentioned above, are liable to vary a little from time to time.

Finally, the mixing and grinding of paints and colours cannot be too well done, as these operations materially influence their brilliance and covering power.

CHAPTER XII.

PAINT VEHICLES.

THE most convenient way of applying pigments to the surfaces of bodies is by mixing them with certain fluid bodies called "vehicles," which act both as carriers and as fixers. Vehicles may consist either of a single fluid, of a mixture of liquids, or even of a liquid containing a solid body in solution, which may act as the real fixing agent, the fluid simply acting as a solvent for this and a convenient medium wherewith to mix the pigment with it for use as a paint. The usual vehicles are certain oils, turpentine, shale spirits, benzoline or petroleum spirit, benzol, coal-tar naphtha, methylated spirit or alcohol and water. Each of these is used in certain classes of paints and varnishes.

PAINT OILS.—The oils are a numerous group of bodies derived from both animal and vegetable sources. The characteristic features of oils are that they are lighter than and insoluble in water, are rather viscid fluids, are greasy to the feel, and impart a permanent greasy stain to paper; they are only partially soluble in alcohol, but are freely soluble in ether, petroleum spirit, and turpentine, and some other solvents of a similar character. Boiled with caustic soda (sodium hydroxide), they are decomposed, yielding soap and glycerine. All the oils are not suitable for use as paint oils; they may be divided into two principal groups with some sub-groups:—1st, Those oils which on exposure to the air do not change, or, at most, become slightly more viscid. 2nd, Those oils which on exposure to air gradually become hard and dry; these oils are called the drying oils, and are used as paint oils on account of their possessing this important property. The first group of oils are known as the non-drying oils; they are quite useless as paint oils, and are never used for that purpose.

The oils belong, chemically, to that group of bodies known as salts, which may be defined as compounds containing two radicles, one of which is of acid origin, the other of basic origin.

In the case of oils the latter is always the body known as

glyceryl ($C_3 H_5$), which when combined with hydroxyl ($H O$) forms the well-known compound, glycerine, $C_3 H_5 (H O)_3$; hence oils are frequently known as glycerides because on saponification they yield glycerine. In the oils this glyceryl is united with various acids; for, while there is only one base present in any oil, there is rarely less than two acids present, and often there are many more. These acids are known as the fatty acids, and form a rather numerous group, or rather several groups of bodies. Some of these, such as oleic, stearic, palmitic, linoleic, are found present to a greater or less extent in all oils; others, such as arachidic, ricinoleic, valeric, &c., are only found in small quantities, and often only in certain oils of which they are the characteristic constituent, such as ricinoleic acid in castor oil, arachidic acid in ground nut oil, valeric acid in fish oils, rapic acid in rape oil, linoleic in linseed oil.

The fatty acids may be divided into three groups, which, from the most prominent acid they contain, may be named—1st, the stearic acids; 2nd, the oleic acids; 3rd, the linoleic acids.

The first group is a very numerous and important series of acids, and is often called, from the most important member of the series, the acetic acid group. Many of these bodies, such as acetic acid and stearic acid, are used on a large scale in various industrial operations; others are of importance as occurring in products which are of great industrial value. The following lists comprise all the known members of these series:—

1. STEARIC SERIES OF FAT ACIDS.

Name.	Formula.	Name.	Formula.
Formic, . . .	$H C H O_2$	Pentadecatoic, .	$H C_{15} H_{29} O_2$
Acetic, . . .	$H C_2 H_3 O_2$	Palmitic, . . .	$H C_{16} H_{31} O_2$
Butyric, . . .	$H C_4 H_7 O_2$	Margaric, . . .	$H C_{17} H_{33} O_2$
Caproic, . . .	$H C_6 H_{11} O_2$	Stearic, . . .	$H C_{18} H_{35} O_2$
Enanthylic, . .	$H C_7 H_{13} O_2$	Arachidic, . . .	$H C_{20} H_{39} O_2$
Caprylic, . . .	$H C_8 H_{15} O_2$	Medullic, . . .	$H C_{21} H_{41} O_2$
Pelargonic, . .	$H C_9 H_{17} O_2$	Behenic, . . .	$H C_{22} H_{43} O_2$
Capric, . . .	$H C_{10} H_{19} O_2$	Lignoceric, . . .	$H C_{24} H_{47} O_2$
Cocinic, . . .	$H C_{11} H_{21} O_2$	Geoceric, . . .	$H C_{26} H_{51} O_2$
Lauric, . . .	$H C_{12} H_{23} O_2$	Cerotic, . . .	$H C_{27} H_{53} O_2$
Tridecatoic, . .	$H C_{13} H_{25} O_2$	Melissic, . . .	$H C_{30} H_{59} O_2$
Myristic, . . .	$H C_{14} H_{27} O_2$		

Formic and acetic acids are liquids having a powerful acid odour, are soluble in water, and can be distilled without change.

The next few members of the series are liquids more or less soluble in water, and can be distilled without change; they have a slight odour of rancid fat, and are known as the soluble fat acids, being present in such fats as butter, cocoa nut oil, and palm nut oil, and are occasionally found present in small quantities in fish oils. The higher members of the series, or from capric acid upwards, are solids; they are insoluble in water, and cannot, as a rule, be distilled without being decomposed.

The fat acids are soluble in alcohol, ether, turpentine and similar solvents; they are monobasic acids combining with one equivalent of potassium hydroxide (caustic potash) or sodium hydroxide (caustic soda) to form soaps, which are more or less soluble in water, the salts of the lower fatty acids being freely soluble, while those of the higher acids are rather difficultly soluble, the solubility decreasing with the complexity of the fatty acids.

2. OLEIC SERIES OF FATTY ACIDS.

Name.	Formula.	Name.	Formula.
Acrylic, . . .	$\text{H C}_3 \text{H}_3 \text{O}_2$	Physetoleic, . . .	$\text{H C}_{16} \text{H}_{29} \text{O}_2$
Crotonic, . . .	$\text{H C}_4 \text{H}_5 \text{O}_2$	Hypogæic, . . .	
Angelic, . . .	$\text{H C}_5 \text{H}_7 \text{O}_2$	Gæidic, . . .	$\text{H C}_{18} \text{H}_{33} \text{O}_2$
Pyroterebic, . . .	$\text{H C}_6 \text{H}_9 \text{O}_2$	Oleic, . . .	
Damaluric, . . .	$\text{H C}_7 \text{H}_{11} \text{O}_2$	Elaidic, . . .	$\text{H C}_{19} \text{H}_{35} \text{O}_2$
Damollic, . . .	$\text{H C}_{13} \text{H}_{23} \text{O}_2$	Doeglic, . . .	
Moringic, . . .	$\text{H C}_{15} \text{H}_{27} \text{O}_2$	Brassic, . . .	$\text{H C}_{22} \text{H}_{41} \text{O}_2$
Cimicic, . . .		Erucic, . . .	

These acids are very characteristic of fats and oils; oleic is by far the commonest of all fat acids, as when combined with glyceryl it forms olein, the fluid constituent of almost all oils. The lower members are more or less soluble in water and volatile by heat without decomposition; the higher members are insoluble, and are decomposed by heat.

3. LINOLEIC SERIES OF FAT ACIDS.

Name.	Formula.
Linoleic,	$\text{H C}_{16} \text{H}_{27} \text{O}_2$
Homolinoleic,	$\text{H C}_{18} \text{H}_{31} \text{O}_2$
Ricinoleic,	$\text{H C}_{18} \text{H}_{33} \text{O}_3$

Linoleic and homolinoleic acids are characteristic of linseed and other drying oils, while ricinoleic acid, which has properties very different from other acids, is found only in castor oil.

Both the oleic and linoleic series of acids are monobasic, like the stearic series, and combine with potash and soda to form soaps which are rather more soluble in water than the soaps made from the stearic acids.

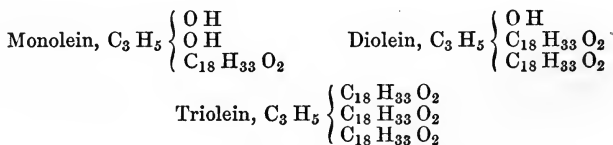
Glycerine, the sweet spirit of oils, is a water-white, very viscid liquid, quite odourless, but possessing a sweet, though metallic, sort of taste. It is heavy, having, when pure, a specific gravity of 1.270. When heated it volatilises with difficulty, being slightly decomposed during the operation. It will only burn when heated, and then with a smoky flame having a small amount of luminosity.

It has a great affinity for water, with which it mixes in all proportions, and which it absorbs from the atmosphere in no small proportions, being strongly hygroscopic. On this account glycerine gradually becomes weaker when exposed to the air. It is soluble in alcohol.

Glycerine is a compound of the basic organic radicle glyceryl ($C_3 H_5$), with three equivalents of hydroxyl, $O H$, and has the

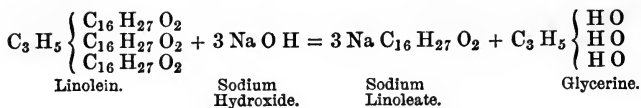
formula $C_3 H_5 \left\{ \begin{array}{l} O H \\ O H \\ O H \end{array} \right.$ It possesses alcoholic properties, and is

capable of combining with acids; with monobasic acids it requires three equivalents to form saturated salts, and hence is capable of forming three different compounds with such acids; thus, with oleic acid it forms—



in which one, two, or three equivalents of hydroxyl are replaced by one, two, or three equivalents of oleic acid. These compounds can be formed by the direct union of oleic acid and glycerine, and it is of interest to note that the triolein so made is indistinguishable from the olein which is present in oils.

When oils are boiled with solutions of caustic soda or potash they are decomposed. A compound of alkali and fat acid is formed while glycerine is liberated. This reaction is shown in the following equation:—



This reaction is known as saponification, because the alkaline compound obtained forms the familiar article, soap.

As stated above, the oils are divisible into two groups—non-drying and drying oils. The former group is by far the larger of the two, but the oils in it are of no use to the painter. The latter group, which is the one which will be dealt with in this chapter, is small in number, but it contains oils of great importance to the painter.

THE DRYING OILS.

There are but few oils, compared with the great number known, that can be used for painting on account of their possessing the essential property of becoming hard or drying when exposed to the air. The best drying oils are obtained from vegetable sources, although one or two are obtained from animal sources. The following list includes all that can be included within this group:—

Linseed oil.	Hempseed oil.
Poppy seed oil.	Tobacco seed oil.
Weld seed oil.	Walnut oil.
Firseed oil.	Japanese wood oil.
Menhaden oil.	

A few other oils, such as niger seed oil, cress seed oil, grape seed oil, cotton seed oil, possess weak drying properties, but these are of much too weak a character to permit of their being used as paint oils. Rosin oil is also offered as a paint oil, but it is not a good drying oil; it will be dealt with in detail further on.

The most important of this group of oils is linseed oil, which is the painter's oil *par excellence*; the others are only used in painting on a comparatively small scale, and mostly by artists, not because they are any better drying oils than linseed, but because they have a paler colour, and, therefore, do not affect the tints of the colours quite so much—a matter of some importance when delicate tints have to be painted. For house-decorating purposes no other oil is used, because no other is so cheap or abundant.



LINSEED OIL.—This oil is obtained from linseed—*i.e.*, the seeds of the flax plant, *Linum usitatissimum*—which is cultivated both for its seed and for its fibre, which latter is spun and woven into linen. Ireland, England, Holland, Germany, Russia, America, Canada, and India are noted for the cultivation of the flax plant, which will grow anywhere where the climate is not too hot, but a cold or temperate climate suits the plant best.

Linseed is a small seed of a flat oval shape, somewhat pointed at one end; it is lustrous, and of a pale brown colour. It varies a little in shape and colour, according to the locality in which it is grown, and an expert can tell by inspection without much error from whence a particular parcel of seed has come. It is exported in large quantities from Riga, Libau, Taganrog, and other Russian ports, and from Calcutta in India. Smaller quantities come from other places, but these occupy only a minor position compared with the seed coming from the places named above. Three qualities of linseed are recognised in the trade—Baltic seed, which comes from Riga and other ports on the Baltic coast of Russia, and is the seed of flax grown in the north of Russia; Black Sea seed, coming from Libau, Odessa, and other ports on the Black Sea, and which is the seed of flax grown in Southern Russia; and East India seed, which is exported from Calcutta. The Baltic seed yields the best and most valuable oil, that from Black Sea seed is next in quality, while East India seed gives oil of inferior quality.

The oil obtained from seed grown in America, Canada, and other places, is mostly used locally, and very little finds its way to the English market. The seed imported is rarely free from other seeds such as those of hemp and rape.

Extraction of Linseed Oil.—The oil is obtained from linseed and other seeds by a process of pressing; but, before being pressed, the seeds undergo some preliminary treatment, with the object of facilitating the process of oil extraction. Naturally the process of extracting oil has undergone many changes during the last fifty years, and for the purpose of this work, it will be sufficient if the modern systems only are described in outline; for further details, the companion work on *Lubricating Oils* in this series of text books may be consulted.

Two systems of oil extraction are used—*viz.*, the English and the Anglo-American; these do not differ very much from one another.

The English system includes five operations:—1st, crushing; 2nd, grinding; 3rd, heating; 4th, pressing; 5th, refining.

1st, *Crushing.*—Prior to this, however, the seed is sifted

through sieves, with the object of separating out as much dirt and foreign seed as possible; this is a preparatory operation, common and essential to all systems of oil pressing, as the presence of much oil from other seeds is apt to spoil the linseed oil. As the majority of the foreign seeds found in the crude linseed are rather smaller than linseed itself, nearly all are separable by using sieves of a certain gauge of mesh.

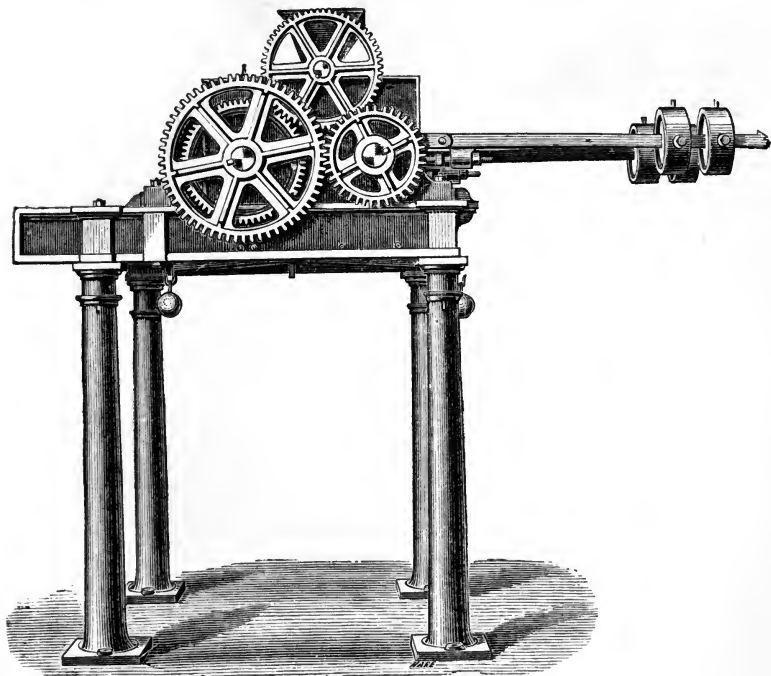


Fig. 55.—Oil seed crushing mill.

The sifted seed is now passed through a crushing machine, which consists of a pair of heavy wheels placed horizontally in a strong frame (Fig. 55). One of these wheels is 4 feet in diameter, and is driven by the one to which power is applied; the other wheel, one foot in diameter, is generally driven by friction from the larger wheel, but in some makes of the mills by gearing; by means of a system of screws and springs in

connection with the bearings of the small wheel, a regulated pressure can be brought to bear on any seed which passes between the two wheels. The large wheel is driven at about fifty-six revolutions per minute. A hopper placed above the wheels supplies the seed in a regular manner, which is crushed in passing between the wheels, and falls into the receptacle

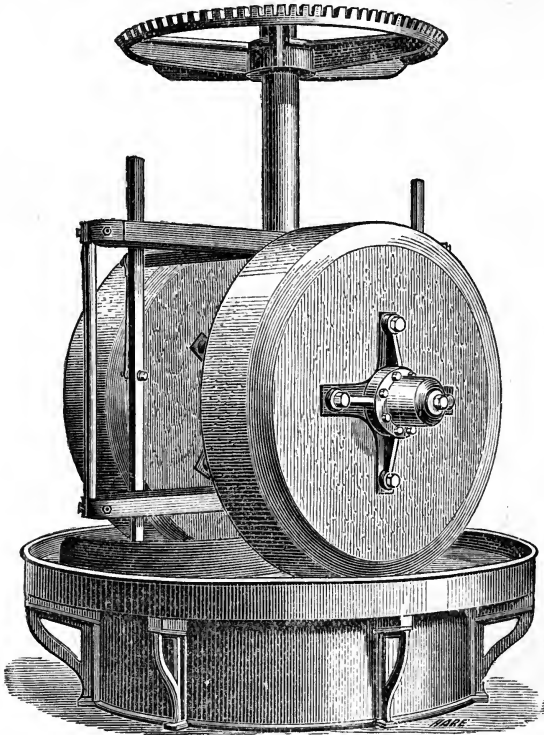


Fig. 56.—Oil seed crushing mill.

placed underneath the machine for the purpose of collecting the crushed seed. Attached to each wheel is a scraper for keeping the surface of the wheel free from crushed seed.

2nd, Grinding.—From the crushing machine the seed passes to the grinding mills, which are of the edge-runner type (Fig. 56), and consists of a pair of large stones, about 7 feet in diameter,

and 16 inches thick, revolving in a rather flat-shaped pan. The stones weigh about 7 tons, and have a speed of about 17 revolutions per minute. In this mill, the seed is ground for about 20 minutes, a little water being usually added. After it has passed through the edge-runner mill, the seed is in the form of a fine pasty mass.

3rd, Heating.—After being ground under the edge-runners, the seed is placed in a kettle, a cylindrical vessel made of copper, and jacketed, so that the inner portion and the seed it contains can be heated; agitators worked by suitable means are also provided to ensure that every part of the seed is heated. In this kettle the seed is kept for 20 minutes at a temperature of about 150° to 160° F. This heating of the seed serves two useful objects; it liquefies the oil, and so causes it to flow more freely from the seed while being pressed; and it causes the coagulation of the albuminous and mucilaginous matters contained in the seed, and so prevents these from flowing out of the seed during the pressing.

4th, Pressing.—The hot seed from the kettle is placed in woollen bags, large enough to hold about 8 lbs. of seed; these are first placed in horse-hair cloths, generally known as “hairs”; and then between the press-plates of an hydraulic press, where they are subjected to a pressure of about 740 lbs. on the square inch for 20 minutes, followed by a pressure of about 2 tons for 7 minutes; during the whole period, oil flows out from the seed and into suitable vessels which have been placed ready to receive it.

5th, Refining.—The oil as it flows from the press is far from being pure and bright; to ensure these qualities it undergoes a process of refining, the details of which vary in different works. First, it is usually placed in large tanks and heated by means of a steam coil to about 160° or 170° F.; this makes the oil more fluid, and causes the coagulation of any albumen which may have passed out of the seed; it is allowed to stand for some time, until all the solid impurities have settled, leaving the oil fairly bright; occasionally it is sold in this condition, but generally it is subjected to a further treatment, which consists in mixing it with 3 per cent of sulphuric acid, previously mixed with an equal quantity of water; the two bodies are thoroughly mixed together and then allowed to stand for 24 hours, when the acid will have settled to the bottom, leaving the oil at the top; the acid layer is run off, and the oil washed free from any traces of acid by means of warm water; it is then ready for use. The sulphuric acid has the property of acting upon any albuminous

or mucilaginous matter contained in the oil, charring and dissolving it, thus carrying it out of the oil, leaving the latter in a purer condition, and, by removal of bodies which are prone to decomposition, rendering the oil less liable to grow rancid; while in other respects its properties are materially improved. The oil as thus made is sold as "Raw Linseed Oil."

The Anglo-American system is comparatively of recent introduction, but already it is most extensively adopted and will in all large oil mills be used exclusively. Like the English system it includes five operations, some of which resemble those of the system just described, while others are different:—1st, crushing; 2nd, heating; 3rd, moulding; 4th, pressing; and 5th, refining.

1st, *Crushing*.—This operation is done by means of a crushing

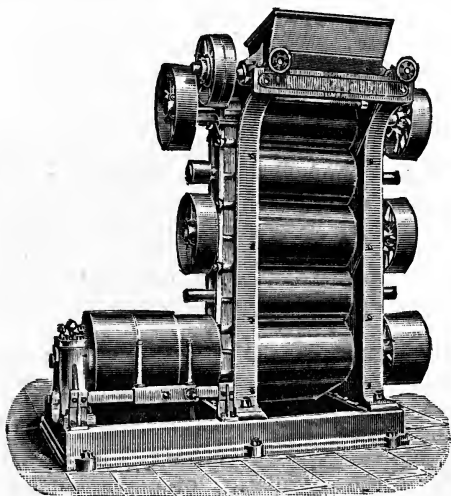


Fig. 57.—Oil seed crushing rolls.

mill, shown in Fig. 57, which consists of a number (usually five) of chilled iron rolls placed one above another in a strong iron frame; the size of the rolls varies according to the required capacity of the machine, but a usual size is two feet six inches long, and one foot in diameter. The seed is fed by means of a hopper between the first and second rolls, and passing between the nip of these receives a first crushing; then, passing round the second roll and between the second and third rolls, it receives a second crushing as it passes through the nip of these rolls; the

crushing weight now exerted on it is greater than at first, the weight of the first roll in the first crushing being augmented by that of the second roll in the second crushing. As some of the crushed seed may adhere in the form of a cake on the surface of the rolls, scrapers are provided to scrape any such seed off the rolls and guide it through the various nips. In the same way as it has passed through the first, second, and third rolls, the seed passes through between the nips of the other rolls, being further crushed in so doing, the weight to which it is subjected increasing as it passes through the various nips; in a roll machine having rolls of the size given above, each roll will weigh about $1\frac{1}{2}$ tons, so that if there are five rolls, the final pressure on the seed will be from $5\frac{1}{2}$ to 6 tons. The seed is crushed by such a set of rolls in a very perfect manner, much better than in the older system of a pair of rolls and an edge-runner grinding mill, and less labour is required.

2nd, Heating.—From the crushing mills the seed passes to the kettle, the construction of which is shown in Fig. 58; here the seed is heated to a temperature of 170° F. for 20 minutes. Steam is sent into the interior of the kettle to moisten the seed and to improve its condition for yielding oil during the pressing.

3rd, Moulding.—From the bottom of the kettle the hot seed is passed into a measuring box holding some 18 lbs. of the crushed seed; thence it passes to the table of a moulding machine, Fig. 58, where it is moulded into a cake of a certain size depending upon the size of the press plates, but usually having a thickness of $1\frac{1}{2}$ inch, the machine exerting a small amount of pressure to bring the mass of meal to this thickness. The surplus seed is returned to the kettle or the crushing rolls to be passed through with fresh seed.

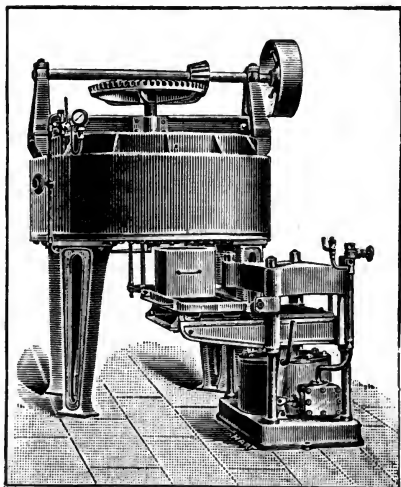


Fig. 58.—Seed kettle and moulding machine.

4th, Pressing.—After leaving the moulding machines, the cakes of meal are placed between two corrugated iron plates hinged together like the backs of a book. In the Anglo-American process the use of hairs and cloths are dispensed with, thus effecting no little economy in the process of oil extraction,

for the hairs and cloths were an expensive item in the older processes, as frequent renewals were required. The press plates, besides being corrugated, are often marked with various letters and other marks, which, being impressed upon the cakes of meal, serve to show what firm pressed the oil cake.

A number of the press plates and their contents are placed in the hydraulic press and subjected to a pressure of from $\frac{3}{4}$ to 1 ton on the square inch, for from 20 to 25 minutes, during which time most of the oil comes from the seed. It is a matter worth noting that the oil passes out from the seed cake along the edges and never from the sides of the cake. After being subjected to a pressure of about a ton for 25 minutes, the pressure is in many works increased to about 2 tons, at which it remains for 5 to 7 minutes, then, when all the oil has flowed out of the seed, the

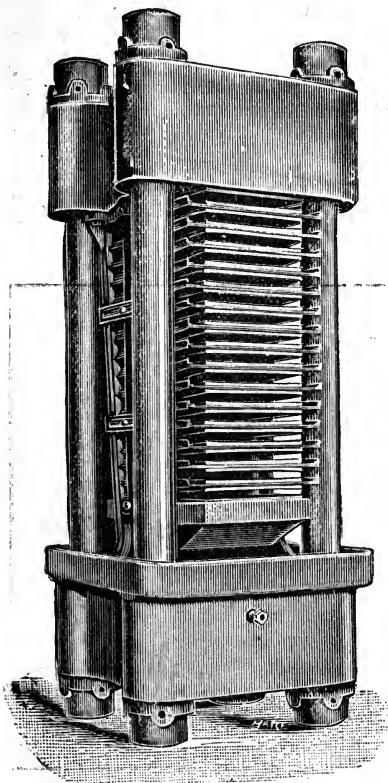


Fig. 59.—Hydraulic oil press.

pressure is taken off, the press plates removed from the press and the oil-cakes taken out; these are sold for feeding cattle, for which purpose they are of great value. The oil flows into tanks, from which it is pumped into large storage tanks, where it is stored until required for further treatment. It is interesting

to note that an intermittent pressure, such as is given by the old stamper press and in the modern forms of hydraulic oil presses, gives far better results than a steady uniform pressure.

Fig. 59 represents the form of hydraulic press made by Messrs. Rose, Downs & Thompson, Hull, to whom we are indebted for the various illustrations of the crushing of linseed.

5th, Refining.—This is done in exactly the same way as in the English system, which see.

Properties and Composition of Linseed Oil.—Linseed oil is sold in two forms, known as “raw” and “boiled” linseed oil; some text-books speak of a third form called “refined linseed oil,” but the author considers this to be only a variety of the raw oil. Linseed oil as it comes from the press is rather turbid, of a dark colour, and contains some albuminous and mucilaginous matter. Before it is fit for use as a paint oil these must be removed, which is done by the methods detailed above; then it forms the “raw linseed oil” of commerce. The “refined” linseed oil is mostly prepared for artists’ use, and is obtained from the raw oil in various ways.

In some cases the oil is allowed to stand for some months to settle, and then the clear top oil is exposed in closed glass vessels to sunlight to bleach it. Sometimes a small quantity of litharge or acetate of lead is mixed with the oil, and then, after standing some time, the oil, which is clear, is run off and bleached as before; in other cases metallic lead is placed in the oil and left in contact with it for months; the lead seems to exert a kind of bleaching action, and at the same time causes the albuminous matter in the oil to settle out.

It may be laid down as a principle in treating oils that the simplest plan is always the best; in any case the use of too much chemical action should be avoided.

Raw linseed oil is a yellowish oil, having a brown hue, and possesses a characteristic odour and taste unlike those of any other oil. It is perfectly clear and limpid at all ordinary temperatures, but when subjected to moderate cold it thickens slightly, and solidifies at a temperature below—27° C. The viscosity of linseed oil measured in Hurst’s standard viscosimeter at 70° F. is for the three principal varieties:—

Baltic oil,	105
Black Sea oil,	108
East India oil,	112

The specific gravity of linseed oil at 60° F. (15°·5 C.) averages 0·935, but ranges from 0·932 to 0·937; Baltic oil is usually the heaviest. A sample of Baltic oil examined by the author had a

specific gravity of 0.9378, a sample of Black Sea oil a specific gravity of 0.9326, while a sample of East Indian oil had a specific gravity of 0.9339. At 212° F. (100° C.) linseed oil usually has a specific gravity of 0.8801.

Linseed oil is soluble in about 40 times its volume of alcohol at ordinary temperatures, and 5 times its volume at the boiling point. It readily dissolves in ether, petroleum spirit, shale naphtha, turpentine, chloroform, and similar solvents.

Sulphuric acid has a strong action on linseed oil, causing it to become thick and of a dark colour; large quantities of sulphur dioxide are evolved, while the temperature of the mixture is considerably increased, the amount varying somewhat in different kinds of linseed oil. Thus, with Baltic linseed oil the author obtained an increase of 120° C., with Black Sea oil an increase of 114° C., and with East India oil an increase of 106° C.

The action of nitric acid varies with the strength of the acid; a moderately strong acid converts linseed oil into a viscid yellowish mass, which is insoluble, or nearly so, in petroleum spirit or benzol; while strong, fuming nitric acid often causes linseed oil to take fire. Nitrous acid does not give a solid elaidin with linseed oil.

In glacial acetic acid it is readily soluble on warming, while the turbidity temperature ranges from 36° C. to 47° C.* according to the quality of the oil and the strength of the acetic acid.

Linseed oil combines very readily with bromine and iodine, absorbing a larger proportion of these bodies than any other oil; there are slight differences between the various kinds of linseed oil in the quantities of iodine and bromine that they will combine with, but it may be laid down as a rule that the better the quality of the oil, the more iodine or bromine will it absorb. Of iodine the average amount taken up is 156 per cent. of the weight of the oil, while of bromine the average is 98 per cent. That is 100 parts of linseed oil will combine with 156 parts of iodine or with 98 parts of bromine.

The property which gives linseed oil its special value as a paint oil is that when exposed to the air it gradually becomes hard, "dries up," in doing which it takes up from the atmosphere a large proportion of oxygen, forming a new compound of a resinous character, the properties of which have never been fully investigated. In this power of combining with oxygen, linseed is distinguished very markedly from other oils, which have little or no power of combining with oxygen. W. Fox† gives the

* Hurst. On Valenta's test for oils. *Journ. Soc. Chem. Ind.*, Jan., 1887.

† *Oil and Colourman's Journal*, 1884, p 234.

following as the number of cubic centimeters of oxygen absorbed by 1 gramme of various oils :—

Baltic linseed oil,	191
Black Sea linseed oil,	186
East Indian Calcutta oil,	126
East Indian Bombay oil,	130
American linseed oil,	156
Brown rape oil,	20
Colza oil,	17·6
Cotton seed oil,	24·6
Olive oil,	8·2

Evidently, the quality of linseed oil depends very much upon its oxygen-absorbing powers ; thus, Baltic oil, which dries better than any other variety of linseed oil, takes up more oxygen than Black Sea or East Indian, which latter takes up the least, and is the worst variety of linseed oil known. American linseed oil is not equal to Black Sea oil in its drying properties, but it is much better than East Indian, owing, as is clear, to its greater absorbing power for oxygen.

Raw linseed oil when exposed in the form of a thin film to the air, as it would be in painting, takes about two days to become thoroughly dry and hard ; the coat left is firm and elastic, but has not much lustre or gloss.

When linseed oil is heated with caustic soda or caustic potash, it undergoes saponification, the amount of alkali required being from 13·4 to 14 per cent. of caustic soda, and 18·7 to 19·5 per cent. of caustic potash, while about 9·4 to 10 per cent. of glycerine is liberated. When the soaps so produced are treated with dilute sulphuric acid they are decomposed, and the fatty acids of the linseed oil are liberated. These acids have a specific gravity of from 0·924 to 0·927 at 15° C., and from 0·861 to 0·864 at 100° C. They are solid acids, melting at 22° to 25° C., and solidifying at from 20° to 18° C., are insoluble in water, but readily soluble in alcohol, glacial acetic acid, ether and other similar solvents. Their combining equivalent is about 306, which points to the presence of acids of complex composition.

Although the composition of linoleic acid (the characteristic acid of linseed oil) is usually given as $C_{16}H_{28}O_2$, recent researches have thrown some doubt on the correctness of this formula. It may be pointed out that the combining equivalent of the fatty acids is 306, that is more than is indicated by an acid having 16 atoms of carbon in its molecule. Allen has considered linseed oil to contain an acid which has 18 atoms of carbon ; he has named it homolinoleic acid, but gives no further details. If linoleic

acid contains 16 atoms of carbon, it is isologous with palmitic acid, and should on being hydrogenised, that is being acted upon in such a manner that it takes up hydrogen, yield palmitic acid; while, as a matter of fact, it forms stearic acid, which is an acid containing 18 atoms of carbon. Then again linoleic acid when subjected to the action of alkaline permanganate of potash yields sativic acid, which is an hydroxy acid having the composition shown by the formula $C_{18}H_{32}O_2(HO)_4$. According to more recent researches linseed oil contains two acids. One is named linolic acid, and has the composition $C_{18}H_{32}O_2$. It is a tetrolic acid, being capable of combining with 4 atoms of bromine. This acid yields sativic acid on oxidation with alkaline permanganate of potash. The other acid has received the name of linolenic acid, has the composition $C_{18}H_{30}O_2$, and belongs to a series of acids having the general formula $C_nH_{2n}-6O_2$, a series not hitherto described. This acid has a high iodine value 245, as might be expected from its being capable of combining with 6 atoms of iodine, or the same number of atoms of bromine.

BOILED LINSEED OIL.—The property which gives linseed oil its peculiar value to the painter is that it absorbs oxygen from the atmosphere when it is exposed in thin films or even in large masses, thereby forming the body known as oxylinoleic acid; this is capable of further oxidation to a body known as linoxyn, which has a composition indicated by the formula $C_{32}H_{54}O_{11}$, and has some valuable properties, being quite neutral in its reactions, more or less transparent, and somewhat elastic. It is quite insoluble in water, alcohol, or ether, but is slightly soluble in chloroform. By long boiling with caustic potash it is saponified, forming a red soap. This body is the final oxidation product of linseed oil when exposed to the air. Oxidised oil can, by means of solvents, be separated into two products; one is insoluble, and the other is soluble. The insoluble body is, when freshly prepared, colourless, transparent, and gelatinous; when dried it becomes a friable yet elastic solid. The soluble compound forms a coloured sticky mass resembling indiarubber, and for which it might act as a substitute. This property of absorbing oxygen is increased by heating the oil to a temperature of 400° or 500° F. for a few hours; it is still further increased by adding to the oil while it is being heated certain bodies which are known as "driers" (see p. 384). Oil which has thus been heated is known as boiled oil, because it is usually heated in large boilers.

Boiling Linseed Oil.—The boiling of linseed oil is done in several ways; 1st, by fire heat; 2nd, by steam.

Fire boiling of Linseed Oil.—The most usual or common method of boiling linseed oil is by means of fire in ordinary shaped boilers of capacities varying from 100 to 600 gallons. In shape these boilers are similar to those used in laundries, Fig. 60, A. One fault of these boilers is that they do not last very long, owing to the oil, or the acid in the oil, attacking and corroding the boiler. This action is most energetic at the bottom where the flame impinges, and is a very serious matter for those who use large and expensive boilers. An attempt was made to remedy this evil by making the bottom of the boiler thicker than the rest as in Fig. 60, B; but these did not last any longer, while a special evil was introduced, owing to the thick metal retaining the heat so long that simple withdrawal of the fire did not prevent the oil boiling over, as it does in the case of the thin-bottomed boilers. In all large oil boiling works, the boilers are made of wrought-iron boiler-plate of the form shown in Fig 60, C; in this form the boiler is made of a uniform thickness of plate, and the bottom, which is made separately, is rivetted to the sides. As the corroding action is confined to the bottom and to the rivets, these can easily be replaced when required; so that these boilers will last longer than the other forms. The boilers are set in the furnace in the usual way.

It is best, however, in all cases, to set the furnaces against the wall of the boiling shed, and to place the fireplaces for feeding the furnaces outside the shed, so that, should the oil boil over during the process, there is less risk of a conflagration

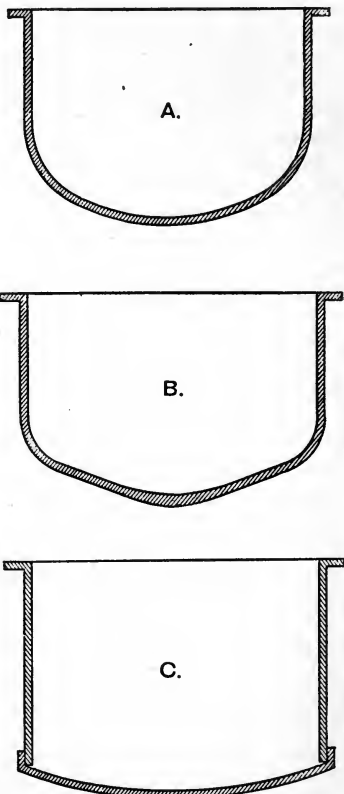


Fig. 60.—Oil boilers.

from the oil finding its way into the fire. The fumes from the boiling oil should not be allowed to inconvenience the workmen, but should be conveyed to a hood placed over the boiler and connected with the chimney of the works.

The boilers should be about one third larger than the quantity of oil which they are to boil, so as to allow room for expansion of the oil, and for any frothing or effervescence of the oil which may take place.

The process of oil boiling is comparatively simple in principle, yet some difficulties crop up now and again in practice; some of these are due to the quality of the oil, others are due to various obscure causes.

The oil is placed in the boiler, which should never be more than two-thirds full, and the fire lighted. While the temperature of the oil is rising, the fluid should be closely watched as it is then that effervescence is likely to take place, and the oil to boil over with possibly disastrous results. Should there be any sign of the oil boiling over to too great an extent, then the fires should be withdrawn, and, by beating the oil, or ladling it out into another boiler, efforts should be made to keep down the effervescence. Much of this is due to the presence of small quantities of water and mucilaginous matter in the oil, and it more often occurs with fresh pressed oil than with oil which has been kept for some time after pressing, and from which, therefore, the water and mucilaginous matter has had a chance to settle out. After some time, dependent upon the quantity of oil being treated, and the size of the fire, the oil begins to enter into quiet ebullition; this is said to be the boiling of the oil; it occurs usually at a temperature of about 500° F. The heating of the oil to this temperature should not be too rapid, so as to give the oil every chance of becoming oxidised, and it should not take less than two hours; a longer time is preferable. When the oil has reached the boil, or better, after it has been boiling for about half an hour, a small quantity of driers is added; other additions are made at short intervals during a period of three hours. The total amount of driers added varies a little in different works, but it averages about 5 lbs. to 1 ton of oil. After all the driers have been added, the oil is boiled for one hour longer; then the fire is drawn and the oil allowed to stand over night to cool and settle. The clear oil at the top is sent into the warehouse, and sold as "boiled oil," while the turbid oil at the bottom is known as boiled oil foots, and is used in making putty or putting into cheap ready mixed paints. It is not advisable to add the whole of the driers, small as it is in proportion to the oil, to the latter all at

once, as the action between the two might become too great, and the oil enter into rather violent ebullition, which could not be controlled readily; by adding in small quantities at a time the action between the driers and the oil is less energetic and the boiling more under control; besides that, the combination between the driers and the oil is more complete.

During the process of boiling oil, the latter undergoes some decomposition. Water is continually being given off, while large quantities of acrolein, C_3H_4O , a derivative of glycerine, which has a powerful action on the lachrymal glands of the eyes, acetic acid, formic acid, and other acids are also given off. As these products are somewhat obnoxious to the workmen, they should be conveyed by means of a collecting hood into the chimney of the works. The oil acquires a dark red colour, due to the presence of some of the products of the decomposition of the oil, although much depends upon the temperature at which the boiling is done. If this is kept below $400^\circ F.$, a comparatively pale coloured oil can be produced; but if allowed to get over $500^\circ F.$, then a dark coloured oil is sure to result. The demand is now for a pale oil, so that in boiling it is desirable to keep the temperature down as low as possible. The quantity and nature of the driers used have some influence on the colour of the oil. Manganese produces a darker oil than any other drier; next to this is red lead and litharge. The acetates of lead and manganese, and the oxalate of the latter metal, produce the palest oils.

It will be found best to give an hour's extra boil at a low temperature, say from 400° to $450^\circ F.$, rather than to heat the oil to $500^\circ F.$ and over, when darkening is sure to occur.

What the character of the action is which goes on during the process of boiling linseed oil is somewhat uncertain. That oxidation occurs is certain, but that is all that is definitely known; probably linoxyn, which may be regarded as the resin of linseed oil, is formed to some extent. Then, when driers are used, there is formed a combination of linoleic acid with the base of the driers, which, dissolving in the rest of the oil, forms a kind of varnish, to which action some of the gloss of boiled oil is due.

The function of driers in oil boiling is undoubtedly twofold. First, they act by increasing the oxidation of the oil, not by yielding up oxygen directly to the oil, because they are added in too small a quantity to have any appreciable action in this respect, but by acting in what is called a catalytic manner, causing by their presence a more ready and complete combination be-

tween the oil and the oxygen of the air. How they accomplish this is not known with certainty, and only the barest assumptions can be made on this point. It is noticeable that the best driers are compounds of bases which can form more than one oxide or more than one series of salts. Lead forms four oxides, manganese forms three well-defined oxides, iron three oxides, while each forms more than one salt with an acid. When such is the case, it often happens that the salts can easily be transformed from one kind to another. Thus, ferrous salts are readily changed into ferric salts and *vice versâ*; manganous salts into manganic salts, and so on. When iron or manganese is used as a drier in oil boiling, it can be conceived that these changes are continually going on, the iron or manganese and lead, if the latter be used, passing from one stage to the other, carrying oxygen from the air to the oil; at the most, however, this is only a theory, and without many facts to support it. The author is not inclined to lay much stress on this theory of the catalytic action of driers.

The decomposition of linseed oil is not complete, because some eight or nine per cent. of glycerine can be extracted from boiled oil.

2nd. *Steam Process of Oil Boiling.*—Besides the ordinary process by means of fire-heat, oil can be boiled by means of steam-heat.

Vincent* describes the following arrangement for carrying out this process. A copper pan (Fig. 61) of sufficient size is provided. This is fitted with a jacket, A, for steam to about two-thirds its depth. Above the pan, and forming a continuation of it, is a dome, in which are three openings, one, B, in the centre for a vertical shaft, S, carrying agitators, C, for the purpose of keeping the oil in constant agitation during the operation. A large opening, D, in the front serves for the purpose of introducing the oil, and observing from time to time the progress of the operation, and for introducing, as required, the driers which are added to the oil. The third opening at the back is fitted with a flue, F, which passes into the chimney, and which serves to carry off any vapours which may be produced. Into the jacket a pipe, T, conveys steam at a pressure of 40 lbs., while another pipe, L, connected with a pump passes into the oil chamber, and is for passing air into the oil.

A very convenient size for such a boiler is one holding about 2 tons of oil.

* *Journal Society of Arts*, 1871.

The plan of working is to first heat the oil in a tank with a closed steam coil for about two hours to a temperature of 95° to 97° C. (203° to 206° F.). This preliminary heating prevents a great deal of frothing in the boiling pan, which is a matter of consequence, especially with Indian oils.

From the tank the warm oil is run into the boiler and the steam turned on in the jacket; after some time the oil begins to emit a peculiar, somewhat sickly odour; then the air is blown

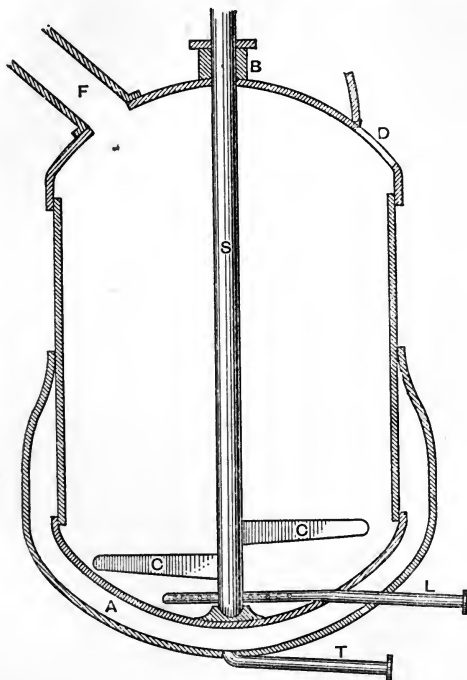


Fig. 61.—Steam oil boiler.

through the oil, when the latter begins to froth a good deal and the odour increases and becomes more pungent. The agitators are kept at work during the whole of the time the oil is being treated. Driers are now added in small quantities at a time until $\frac{1}{2}$ lb. for every cwt. of oil in the pan has been added, this addition taking about two hours; after which the oil is kept

boiling for four hours longer. Then the steam and air is stopped and the oil run into the settling tanks, where it is allowed to remain for from three days to a week to settle. The clear oil is used for making paints, &c., and the foots for putty making. Another steam oil boiler is shown in

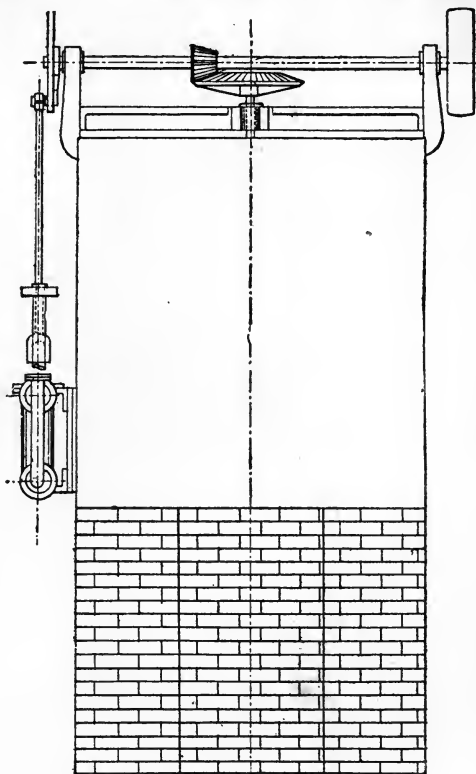


Fig. 62.—Oil boiler.

Fig. 62, and is made by Messrs. Rose, Downs & Thompson. It consists of a jacketted still-pan set on brickwork; in this an agitating gear is fixed, which may either be driven from a separate engine (as shown in the drawing) or from the general shafting of the works. The oil is placed in the pan, the steam turned on and the agitator set in motion; when all effervescence

of the oil has ceased driers are added in small quantities at a time, and the air is blown through by means of an air-pump.

The advantages of using a steam process of oil boiling are that the risk of fire is greatly reduced, and the oil is paler in colour, which is a great consideration, although the character of the driers used will have some influence on this point, acetate of lead and other colourless driers giving the palest oil. For all purposes steam-boiled oil is as good as, if not better than, fire-boiled oil.

Messrs. Hartley & Blenkinsop have patented the production of a heavy drying oil from linseed oil by the following process. A manganese linoleate is made by preparing a soap of linseed oil and adding this to a solution of manganese salt. The manganese linoleate is dissolved in twice its weight of turpentine, and from 2 to 5 volumes of this solution are added to 100 volumes of linseed oil. Insoluble matters are separated, the mass raised to a temperature of 212° F. in a special apparatus, and a current of air or oxygen passed through the oil until it has attained the desired degree of thickness; for example, a clear, transparent oil of a pale amber colour having a specific gravity of 0.997 can be obtained from a linseed oil of specific gravity 0.937. This thickened oil may be used in painting, and in the manufacture of floor-cloth, linoleum, and similar materials.

Properties of Boiled Oil.—Boiled oil is a slightly viscid oil of a reddish colour, varying a little in depth of colour according to the temperature, and the length of time it has been heated in the process of boiling. Its odour is peculiar, and its taste, which is rather acrid, somewhat characteristic. In specific gravity it varies a good deal, but the average is about 0.945; some samples will reach 0.950, while others may be as low as 0.940. Boiled oil is soluble in turpentine, petroleum spirit, shale spirit, benzene, carbon bisulphide and other similar solvents. When boiled with caustic soda or caustic potash it is saponified almost completely; there is usually a small trace of unsaponifiable hydrocarbon oil formed by the decomposition of the oil during the process of boiling.

When exposed to the air in thin layers it dries much more rapidly than raw linseed oil, and leaves behind a hard, lustrous coat; it is this property which makes boiled oil of so much use to the painter; yet it does not do to use boiled oil alone in the making of paints, because the coat which it leaves is too hard and rather liable to crack on exposure to the air; raw linseed oil is always added, as, by leaving a more elastic coat, it prevents this bad fault of boiled oil from showing itself.

Adulteration of Linseed Oil.—Both the raw and boiled

linseed oils are frequently adulterated; (substitutes for boiled oil will be described more fully later on); the principal adulterants used are mineral and rosin oils. Other fatty oils, such as cotton seed, niger seed, and whale oils, are sometimes used; but, as linseed oil is cheap, the small gain arising from their use does not compensate for the probable loss of custom which must ensue if the adulteration be found out; while the great difference in the cost of linseed and mineral oils is a strong inducement for adulterating with the latter.

For the purpose of detecting adulteration the following tests may be applied:—

1. *Specific Gravity*.—For raw linseed oil this should be about 0.932; if less than 0.930, adulteration with fish, seed, or mineral oils would be indicated; while if the gravity exceeds 0.937, then admixture with rosin oil is very likely. The specific gravity of boiled oil averages about 0.945; if much heavier than this it is quite probable that rosin oil has been mixed with the oil; while if below 0.940, then other fatty and mineral oils may be looked for.

2. *Flash Point*.—Linseed oil, whether raw or boiled, flashes at about 470° F. Other fatty oils flash at about the same temperature. Rosin oil flashes at from 300° to 330° F., and during the process of testing a strong odour of rosin would be given off. Mineral oils, such as would be used to adulterate linseed oil, will flash at from 380° to 420° F., so that the flash point is one of the best tests for detecting the adulteration of linseed oil with mineral or rosin oils.

3. *Proportion of Mineral or Rosin Oils in Linseed Oil*.—To determine the proportion of mineral or rosin oils, in adulterated linseed oils, place 20 grammes in a beaker with a little water and alcohol; then add some caustic soda and boil for some time, stirring at intervals; the linseed oil becomes saponified, while the adulterants are not acted on; after about an hour's boil, the mass is allowed to cool a little; then it is poured into a separating funnel and some petroleum ether is added, which will take up the mineral oil and form a layer on the top of the aqueous layer; after allowing the two layers to separate completely, the bottom layer is run off, and the top layer is washed quite free from all traces of the soap formed by the action of the alkali on the linseed oil, by several treatments with warm water. The ethereal layer is then run into a weighed glass, the ether evaporated off, and the residue of mineral oil weighed. Whether the residue is mineral or rosin oil must be judged from the nature of the residual oil after evaporating off the ether; if this is heavy and viscid, and smells of rosin when heated, then rosin oil is present; if the residual oil is light, then mineral oil is present.

4. *Cotton and other Fat Oils in Linseed Oil.*—The detection of cotton seed, niger seed, or other fat oils in linseed oil is much more difficult, but much valuable information on this point will be gained by noticing the behaviour of the oil with strong sulphuric acid, the character of the mass formed, and the temperature which the mixture of acid and oil attains. The character of the soap formed on boiling the oil with caustic soda, the appearance, melting point, and combining equivalent of the fatty acids which may be obtained from the soap so formed are also valuable indications of the character of the fatty oil adulterants.

5. *Driers in Boiled Oil.*—About 25 grammes are boiled with a little dilute hydrochloric acid, with constant stirring, for about half an hour; the mass is allowed to stand to separate; the bottom acid layer contains the driers added during the boiling of the oil, this is run off and tested in the usual way; then the oil is boiled with caustic soda until it is saponified, then the mass is treated in the separating funnel, as described above, to separate the mineral or rosin oil used to adulterate the boiled oil. The aqueous layer which has been run off may be acidified, and the acids obtained tested for rosin by Gladding's test.

BOILED OIL SUBSTITUTES.—Many substitutes are offered for boiled oil, some of which have been patented. In composition they vary greatly, and it is not possible to do more than briefly indicate their general features. Some are mixtures of boiled oil, rosin, turpentine, rosin oil; others more closely approach an oil varnish in composition, being made by melting rosin, then mixing it with hot oil and thinning down with rosin spirit. Some are made by preparing a compound of lime or alkali with rosin or other resinous products, and dissolving this in oil and rosin spirit or turpentine.

The quality of these products varies very much. None of them are equal to good boiled oil, although one or two very nearly approach it; others are but inferior substitutes, and cannot be recommended even for inferior work. It is not possible to deal more particularly with these boiled oil substitutes in this book.

POPPY OIL.—This oil is obtained from the seeds of the poppy (*Papaver somniferum*) by pressure, or it may be extracted by means of solvents. This oil, although a very good drying oil, is not largely used, chiefly because its price does not allow it to compete with linseed oil; artists make use of it on account of its paleness in colour not interfering so much with pale tints as linseed oil does, its price not being so much an object with them as it is with house painters.

Poppy oil is usually of a pale straw colour, very limpid, has little or no odour when fresh, and a pleasant taste; the oil is free from the narcotic properties for which the plant itself is famous. In specific gravity it ranges from 0.924 to 0.927. It solidifies at -18°C . It is soluble in about four times its volume of boiling alcohol and twenty-five times its volume of cold alcohol. Mixed with strong sulphuric acid (Maumene's test), the rise in temperature is about 88° to 90°C . It takes about 19 per cent. of caustic potash (K O H) to saponify it, and it absorbs about 134 to 137 per cent. of iodine.

HEMPSEED OIL.—The hemp plant (*Cannabis sativa*) yields a roundish greenish-grey seed, very familiar to lovers of canaries, from which, on expression, an oil is obtained that is used for painting. The yield of oil varies from 15 to 25 per cent.

Hempseed oil when fresh has a greenish-yellow tint, but on keeping it slowly turns to a brownish-yellow; its odour and taste are rather unpleasant. Its specific gravity ranges from 0.925 to 0.931. It becomes turbid at a temperature of -15°C ., but does not set completely solid until a temperature of -25°C . is attained. Strong sulphuric acid has a vigorous action on it, the increase in temperature being about 100°C . It absorbs from 143 to 144 per cent. of its weight of iodine, which indicates that it contains a large proportion of linoleic acid, and shows that its drying properties must be good.

In this country hempseed oil is rarely used as a paint oil, its price being against it; still, it has been mixed with linseed oil, and it is difficult to obtain the latter free from it, owing to the Russian linseed growers mixing hempseed with the linseed. In Russia, and other places where hempseed is grown, the oil is used rather largely for painting.

WALNUT OIL.—The common walnut, the fruit of the walnut tree (*Juglans regia*) contains about 50 per cent. of its weight of an oil possessing drying properties. The process of extraction of this oil is as follows:—

The nuts are collected and placed in heaps for a period of about three months, when they begin to decompose; they are then crushed and pressed; this gives "virgin nut oil," often used as a food oil as well as a paint oil. The nuts still contain some oil, which is extracted by grinding the cake with hot water and again subjecting it to pressure; the oil so got is known as "fire-drawn nut oil."

Walnut oil is usually of a pale yellowish-green tint, but it can be prepared from fresh kernels almost colourless. The specific gravity varies from 0.925 to 0.927; it begins to be turbid at a

temperature of -15° C., but becomes solid only when at a temperature of -27.5° C. Strong sulphuric acid causes the evolution of some heat, the increase in temperature being 101° to 103° C. It will absorb about 144 per cent. of iodine, pointing to its containing linoleic acid in large proportion.

It is a powerful drying oil; some authorities say that it is superior to linseed oil in this respect; at all events it is quite equal to it in drying power. It is chiefly used by artists, as it is pale in colour, and can, by bleaching, be obtained almost colourless. Its greater cost prevents its coming into extensive use as a substitute for linseed oil in house painting.

ROSIN OIL.—When rosin (the solid residue left by turpentine after all its volatile spirit has been distilled off by the aid of steam) (see p. 362) is distilled in large iron retorts it is decomposed, and five principal products are obtained: 1st, gas; 2nd, pyrolic acid, a watery liquid containing 10 to 12 per cent. of acetic acid; 3rd, rosin spirit; 4th, rosin oil; and 5th, a residue, rosin pitch, which is left behind in the still. The proportions of these bodies obtained depends partly on the nature of the rosin and partly on the method of distillation.

There are two principal methods of distillation. In one, the most used, the rosin is placed in large vertical stills of cast iron capable of holding about 2,000 gallons, the usual charge being 70 barrels of 25 gallons capacity. The still is connected with worm condensers and receiving tanks. When heated by fire the various crude products named above pass over. The proportion of products to the rosin employed varies from time to time, but the following are the average quantities:—

Gas,	5.4 per cent.
Acid water,	2.5 „
Rosin spirit,	3.1 „
Rosin oil,	85.1 „
Pitch,	3.9 „

Sometimes the distillation is carried to dryness, when coke is obtained instead of pitch as the final residue; but, pitch being the more valuable product of the two, this is seldom done.

The operation of distilling takes from 50 to 60 hours, the usual length of time being 56 hours.

The second method of distilling is similar to the first so far as the plant is concerned, but the distillation is carried out with the aid of superheated steam in addition to fire heat. The main products are the same, but there is a larger proportion of spirit and a smaller proportion of rosin oil; the spirit averages about 15 per cent. and the oil about 62 to 64 per cent. of the weight of

the rosin employed, while the amount of acid water is necessarily largely increased by the condensation of the steam passed into the still. This process is not much used.

The rosin spirit is described more fully on p. 372 *et seq.*

The crude rosin oil which comes from the stills varies in appearance and quality at various periods of the process; and also according to the manner in which the operation is conducted. Two varieties of crude rosin oil are recognised; "hard rosin oil," which is chiefly obtained when the distillation is conducted rapidly, and is the product which comes over during the first stages of the operation; and "soft crude rosin oil," which is the product obtained when the process is conducted slowly, and during the middle period of the distillation; sometimes a "medium crude rosin oil" is collected as the final part of the oil to come over.

"Hard crude" is a thick turbid oil of a dark red colour, used for mixing with coal-tar and paraffin greases for making lubricating greases with. As it, when exposed to the air, absorbs oxygen and resinifies somewhat, it has been used as a paint oil, but its use, for reasons which will be pointed out presently, is unsatisfactory.

"Soft crude" is rather thinner than the last; is, if anything, lighter in specific gravity, and is more acid in character. Its chief use is for mixing with lime in the preparation of wheel greases. It does not dry as well as "hard" rosin oil.

The specific gravity of the crude rosin oil varies from 0.996 to 1.030; it has acid properties, due to the presence of an acid or acids, the nature of which is unknown. It takes 0.3 parts of sodium hydroxide to neutralise the acid in 100 parts of the oil. There is much, about 60 per cent., unsaponifiable oil in crude rosin oil.

Crude rosin oil is refined by alternate treatments with sulphuric acid, caustic soda, and redistillation; the oftener these operations are repeated the purer becomes the refined rosin oil obtained; the refining can be carried so far as to yield a product of a very pale colour.

Refined rosin oil is a viscid, oily liquid, varying in colour from dark red to pale yellow in the best refined samples; its specific gravity ranges from 0.980 to 0.995; it has a peculiar odour. Its taste, especially if there is a strong after-taste, is peculiar and characteristic. The cruder varieties have a bluish or bluish-violet bloom or fluorescence, which is less marked in the more highly-refined samples.

The cruder varieties of refined rosin oil contain small quantities

TABLE OF DRYING OILS.

NAME.	Source.	Characters.	Specific Gravity at 60° F.	Iodine Equivalent.	Percentage of K O H required for Saponification.	Rise of Temperature with Sulphuric Acid.
Linseed oil,	Seeds of the flax plant, <i>Linum usitatissimum</i> .	Pale brownish-yellow, peculiar odour and taste (see p. 343).	0·930 to 0·937	156 to 160	18·74 to 19·52	104 to 115°
Hempseed oil,	Seeds of the hemp plant, <i>Cannabis sativa</i> .	Greenish-yellow, peculiar taste and smell (see p. 356).	0·925 to 0·931	...	17·31	...
Poppy seed oil,	Seeds of the poppy, <i>Papaver somniferum</i> .	Straw-yellow to colourless; limpid; slight odour and taste (see p. 355).	0·924 to 0·927	135 to 137	19·28 to 19·46	74
Weld seed oil,	Seeds of the dyer's weld, <i>Reseda luteola</i> .	Dark green; limpid; nauseous taste and odour; good drier.	0·936
Niger seed oil,	From the seeds of <i>Guizotia oleifera</i> .	Pale yellow; rather limpid; slight odour and taste; does not dry well.	0·924 to 0·928	132·9	18·9 to 19·2	82
Walnut oil,	From the walnut, the fruit of <i>Juglans regia</i> .	Greenish to yellowish oil; rather syrupy; nutty taste; good drier.	0·925 to 0·927	...	19·60	101
Scotch Fir seed oil,	From the fruit of the Scotch fir, <i>Pinus sylvestris</i> .	Brownish-yellow oil; rather turpentiney odour; dries well.	0·931
Tobacco seed oil,	From the seeds of the tobacco plant, <i>Nicotiana tabacum</i> .	Greenish-yellow; slight or no odour; mild taste; dries readily.	0·923
Menhaden oil,	From the Menhaden fish, <i>Alosa Menhaden</i> .	Brownish colour; rather turbid oil; fishy odour and taste; dries fairly well.	0·927 to 0·932	...	19·3	126

of free acid and some products capable of combining with caustic soda; the more highly refined products are almost, if not entirely, pure hydrocarbons. The flash point of rosin oil is about 320° F., and the fire point about 390° F. The odour on heating is characteristic of rosin oil.

The cruder varieties of rosin oil possess feeble drying powers, but the more refined oils have none at all. Rosin oil possesses one very objectionable feature in its drying properties; it dries, but in the course of a few weeks the coat becomes soft and tacky or gives again, as the painters say; even if rosin oil paint has been used for a bottom coat and a good linseed oil paint for a top coat this defect will make itself apparent. No means are known by which this defect of rosin oil can be remedied or of increasing the drying power in any degree. The use of rosin oil in paints should, therefore, be avoided.

The addition of rosin oil to linseed oil or other paint oils can be readily detected by the increase in specific gravity, the low flash point, and the odour of rosin on heating; while the amount may be approximately ascertained from the amount of unsaponifiable oil left after boiling with caustic soda.

The other oils are of but slight importance, and the preceding table will give all necessary information about them.

TURPENTINE.—Turpentine is the term which was originally given to some resinous exudations from various species of pine and other coniferous trees, but, of late years, this term has been used to distinguish a volatile liquid obtained from the crude turpentines by distillation; formerly this liquid was known as "oil" or "spirits of turpentine," and occasionally it is now so named; it is also known shortly as "turps." The crude turpentines are but of small value commercially, and some are only used in medicine. There are many varieties, such as Venice, Strasburg, Canadian, Chian, Aleppo, &c. Each of these has a soft resinous character and an aromatic odour; when distilled with steam they are decomposed into a volatile spirit and a solid residue, rosin or colophony. As these bodies are not used in making varnishes no further mention will be made of them.

Under the term turpentine will be described the liquid spirit used by painters and varnish makers.

There are three varieties of turpentine met with in the English market—viz., American, French, and Russian turpentines. All these are derived from various species of pine trees.

American Turpentine is derived from two or three species of pine, chiefly from the swamp or Georgia pine (*Pinus australis*), which grows in extensive forests in North and South Carolina,

Georgia, and Alabama, the former State being the largest producer of turpentine. From the loblolly pine (*Pinus taeda*), turpentine is also obtained.

In winter, which extends from November to March, gangs of men proceed to the forests for the purpose of collecting the resin; for this purpose the trees are boxed, that is, a cavity is cut into the side of the tree, about 1 foot from the ground; the boxes have a capacity of about 2 or 3 pints. Sometimes 3 boxes will be made in a tree, but care is taken not to touch the heartwood, as such a proceeding would certainly kill the tree. The upper part of the box is always kept free from resin, and is frequently chipped so as to expose fresh surfaces of wood, which causes the resin to flow more freely. About March, the sap begins to flow and to collect in the box and on the sides of the cut surface, that which collects in the box is called "dip," and that which collects on the sides is known as "scrape." That which collects the first year in a box is known as "virgin dip," and is always collected separately. The crude resin is known commercially as "gum thus," and is exported for use in making varnishes. Most of the resin is, however, treated locally for turpentine and rosin.

Turpentine is obtained from the crude resin by placing it in a still; into this still passes a steam pipe from a steam boiler, while out of it passes a pipe in connection with a worm condenser; a manhole on the top serves for the purpose of filling the still, while a large pipe at the bottom serves to run off the residual rosin. The still is built into a suitable furnace, so that it can be heated by fire. When sufficient resin has been placed in the still the fire is lighted, and when the temperature has attained a little above the boiling point of water, the current of steam from the boiler is sent in; the turpentine passes over into the worm condenser and condenses along with water from the steam; when no more turpentine comes over, the rosin left in the still is run off into barrels, when the still is ready for another charge. The turpentine is often purified by a second distillation. The appliances in use are generally of a crude description.

The properties of American turpentine will be dealt with shortly.

French Turpentine.—This variety is obtained from the maritime pine (*Pinus maritima*), which grows very extensively in the South-west of France, especially in the Departments of Landes and Gironde. The industry in these districts is conducted on a rather more scientific principle than in America. The trees are cut in February or March, and the sap is caused to flow into an earthenware vessel placed at the foot of the tree.

The trees are tapped for five years in succession, when they are not touched for a few years, and then tapping commences again; when the tree has got somewhat exhausted, the final tapping takes place, and a large yield of resin obtained, but the tree is killed. It is felled, and another planted in its place.

The distillation of the crude resin is carried on in the plant shown in Fig. 63, which is a front view or section of, and Fig. 64, which is a side view or section of the plant. A is a boiler heated by means of a steam coil, or (as shown in the drawing) by means of a fire, the former method being preferable; in this, the crude resin is heated to a temperature of 96° C. (194° F.), when it becomes liquid. The boiler is fitted with a movable cover to prevent the easy escape of turpentine and the entrance of dirt. When the resin is melted, it is run into the tank, B, through the pipe, *a*; the particles of woody tissue, dirt, &c., are deposited in this tank, as also in the boiler, A. From the tank, B, the melted resin is run into a tank, C, which holds the quantity usually treated at one time (about 66 gallons); this tank is, therefore, a measuring tank, from this it runs through the pipe, *b*, into the still, D, which has the form shown; into this passes a steam coil, by which steam from an ordinary steam boiler can be sent into the still. An opening near the bottom of the still (which is kept plugged during the time the turpentine is being distilled), permits of the rosin being run off. E is an ordinary worm condenser fitted into a tub through which cold water is continually passing; with this worm condenser the still is connected by means of a goose neck (shown in the drawing).

The crude resin is placed in the still, 66 gallons being the usual charge; it is then heated by fire until a temperature of 135° C. (275° F.), is attained; when a current of steam is passed into the still, turpentine begins to come over and to condense along with the water from the steam in the worm condenser, the condensed products passing into a suitable receptacle, in which the water gradually settles to the bottom, while the turpentine rises to the surface; the latter is skimmed off and run into other narrow-mouthed vessels, in which it is allowed to stand for several days, during which the remaining water and other impurities settle out. The yield of turpentine is rather more than one-fifth that of the crude resin employed.

When all the turpentine has been distilled over, the residue in the still is run first into a tank, F, and from thence into a revolving screen, G, through which it flows in a fairly clear condition free from dirt and grit of any kind. By this means,

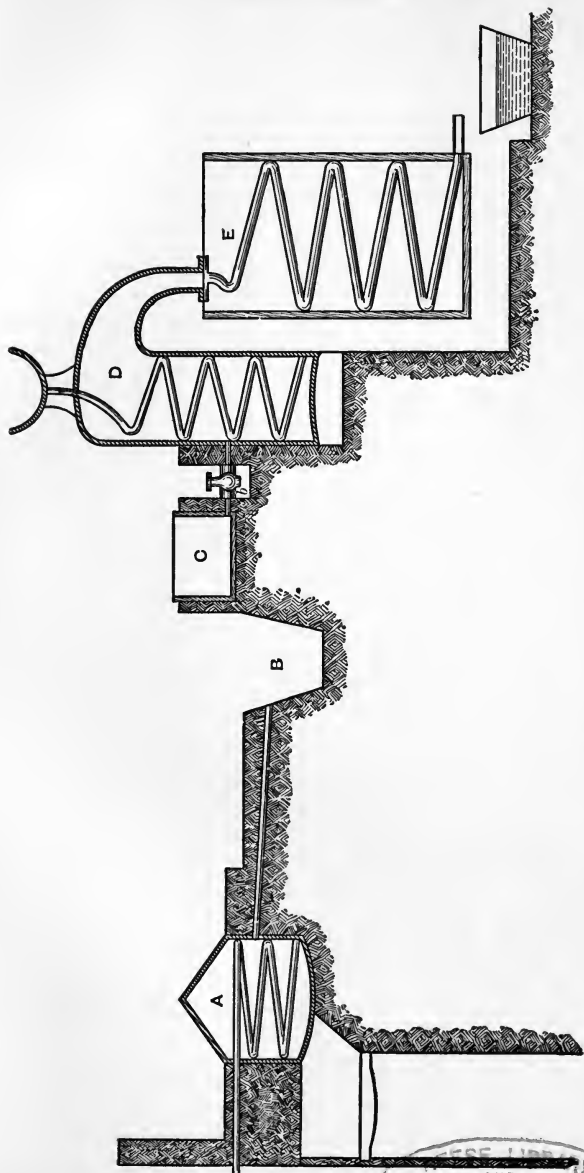


Fig. 63.—Turpentine distilling plant.

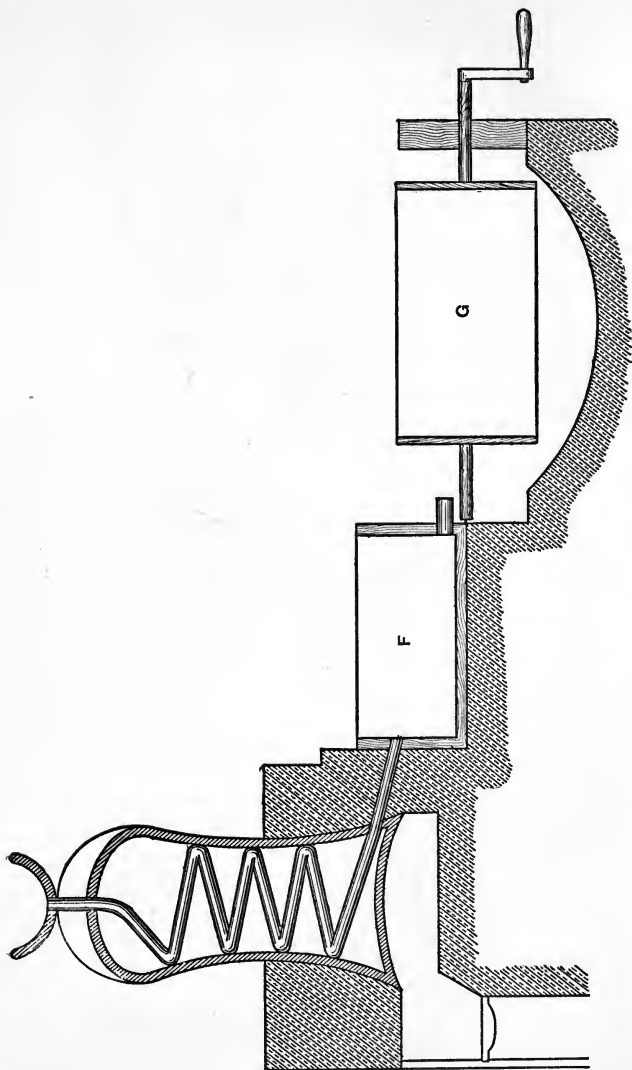


Fig. 64.—Turpentine distilling plant.

too, the rosin is freed from any water it may contain. The quantity of rosin obtained is rather less than four-fifths of the resin used.

French turpentine is almost entirely consumed in France; very little is now exported into England. Its properties will be discussed later on.

Russian turpentine is obtained chiefly from the Scotch pine, *Pinus sylvestris*. The method of obtaining it does not differ essentially from that adopted in extracting American or French turpentine, although there are some minor differences in the method of tapping the trees and collecting the crude resin, and in the manner of distilling the turpentine, which is usually done in a rather crude manner.

Russian turpentine differs slightly in properties from American and French turpentines.

Turpentine is a hydrocarbon having the formula $C_{10}H_{16}$; there are, however, a number of isomeric compounds known which have the composition represented by the above formula. These bodies have been named the terpenes; they are derived, as well as the three varieties of turpentine already described, from natural resins or from various natural oils.

They closely resemble one another in their chemical as well as in many of their physical properties. The terpenes have been investigated by Berthelot, Tilden, Wallach and other chemists, and a number of them are known. Berthelot pointed out that French turpentine had some different properties from American turpentine, although their chemical composition was the same. He named the terpene of American turpentine, australene, and that from French turpentine, terebenthene; while he gave to the characteristic hydrocarbon of Russian turpentine the name of sylvestrene. Armstrong considers that American turpentine is a compound of two terpenes, one of which is the same as found in the French turpentine and which rotates a ray of polarised light to the left; this he names lævoterebenthene. The other terpene has similar properties, only it rotates the ray of polarised light to the right; this he names dextroterebenthene; it is found in a very pure condition in the turpentine from *Pinus Khasyana*, a Burmese tree. Wallach describes nine terpenes which he names—1. *Pinene*, the main constituent of French and American turpentine. 2. *Camphene*, which differs from all other terpenes in being solid; it is not found naturally, but can be prepared by artificial means from pinene. 3. *Fenchene*, which is also obtained artificially. 4. *Cimonene*, found in the essential oils of various species of

aurantiaceæ, oils of lemon, orange, bergamot, &c. 5. *Dipentene*, found in oil of camphor, Russian and Swedish turpentine, &c. 6. *Sylvestrene*, the characteristic terpene of Russian and Swedish turpentine. 7. *Phellandrene*, found in various essential oils. 8. *Terpinene*, found in several oils. 9. *Terpinonlene*, a rare terpene. The two most important of these are Pinene and Sylvestrene, which are found in the chief commercial turpentines.

Pinene is a colourless or water-white mobile liquid of a peculiar and characteristic odour, having a specific gravity of 0.8749 according to Tilden; Wallach gives it as 0.860. It boils at from 155° to 156° C. When dry hydrochloric acid gas is passed into it, combination ensues, and a crystalline body having the formula $C_{10}H_{16}HCl$ is formed; this closely resembles camphor in appearance and is known as artificial camphor; by heating, under pressure, with caustic potash this body is decomposed and the solid terpene, camphene, is formed. When pinene is exposed to sunlight in the presence of water a crystalline compound is formed which has the composition $C_{10}H_{18}O_2$, and is named by Armstrong *sobrerol*. Pinene in contact with water gradually combines with it, forming a crystalline hydrate, terpene hydrate, $C_{10}H_{16} \cdot 3H_2O$, which is soluble in alcohol, insoluble in turpentine, slightly soluble in cold water, a little more freely in hot water, and sparingly soluble in ether, chloroform and carbon bisulphide.

There are two varieties of pinene, which differ from one another simply in their action on a ray of polarised light. One variety, that in French turpentine, turns the ray to the left, and is distinguished as *lævo-pinene*, the other is found in American turpentine, and turns the ray to the right, and is named *dextro-pinene*. The air-oxidation and other products from the two terpenes differ from one another in the same manner. A mixture of the two pinenes, in equal proportions, would have no action on polarised light, and gives rise to inactive oxidation products. American turpentine contains both pinenes, the *dextro* variety predominating.

Sylvestrene is the characteristic terpene of Russian and Swedish turpentine, derived from the Scotch pine, *Pinus sylvestris*. It is a colourless, or water-white limpid liquid, having a specific gravity of 0.846 at 20° C.; it boils at 175° C. It has a *dextro-rotatory* action on polarised light; the *lævo-rotatory* and inactive varieties are not known. Dry hydrochloric acid gas, when passed through sylvestrene, forms an hydrochloride, $C_{10}H_{16}HCl$, which is liquid. In this respect this terpene differs from pinene; it is also more easily oxidised when exposed to air and light.

The other terpenes are of no practical importance to the painter. Commercial French and American turpentine is a water-white, limpid liquid, with a peculiar and characteristic odour that distinguishes it from all other bodies. The specific gravity ranges from 0.864 to 0.870, but usually is about 0.867. French turpentine is a little more uniform than American turpentine in this respect. It begins to boil at from 156° to 160° C., and is completely distilled at 170° C. If the sample be fresh, there is little or no residue left behind, but old samples generally leave a slight residue of resinous matter, which in any case does not amount to more than 1 per cent. of the turpentine.

Turpentine is readily combustible, burning with a smoky flame, a peculiar and characteristic odour being evolved. The flashing point of ordinary turpentine is 36° to 38° C. (97° to 100° F.).

Turpentine is readily miscible with ether, carbon bisulphide, alcohol, benzene, petroleum spirit, but it is insoluble in water. It is a good solvent for oils, fats, resins, &c.

On exposure to the air in bulk, turpentine absorbs oxygen slowly from the atmosphere, becoming thick and viscid or fatty in appearance. A prolonged exposure causes the turpentine to become resinous, part of the turpentine volatilising during the exposure. In thin layers, such as would be formed when turpentine is spread over a surface with a brush, a condition of affairs which occurs in painting, there is less oxidation, as a larger proportion of the turpentine volatilises away, and the oxidation of the residue is more complete, so that a hard resinous product is the result. This property distinguishes turpentine from all the other spirituous liquids used by the painter and varnish maker. These evaporate completely away, and consequently leave no residue behind which can act as a binding agent for the pigment or colouring matter of the paint; whereas, the resin left when turpentine is used, acts as a binding agent, and fixes or fastens the pigment of the paint on the surface over which it is spread. American has greater absorbing powers for oxygen than French turpentine.

Exposed to the air in contact with water, turpentine forms a solid crystalline product, having the composition $C_{10}H_{18}O_2$. This has been named *sobrerol*; the melting point is 150° C. for the active variety, and 130.5° to 131° C. for the inactive variety. The crystals belong to the rhombic system, the inactive variety being of a different form to the active varieties. They are somewhat soft and flexible, and are soluble in alcohol.

When repeatedly distilled with strong sulphuric acid, turpen-

tine becomes polymerised. Generally two bodies are formed. One of these has been named terebene, which has the same formula ($C_{10}H_{16}$) as turpentine, and, when pure, boils at $160^{\circ}C$. The other body has been named colophene, has the formula $C_{20}H_{32}$, and boils at $300^{\circ}C$. It constitutes the main product of the reaction. This property of polymerisation, which is essentially a conversion from a spirit boiling at a low temperature into a spirit boiling at a high temperature, distinguishes turpentine from any of its substitutes.

Nitric acid acts very energetically on turpentine, the result varying with the strength of the acid used. If strong enough, the turpentine may take fire; in any case, various oxidation products are obtained.

Chlorine, bromine, and iodine act with great energy on turpentine; great care must be taken in bringing these bodies into contact with one another or explosions may occur.

Turpentine has a strong action on polarised light, a property which distinguishes it from benzene, petroleum spirit, and rosin spirit. French turpentine rotates the ray to the left, its specific value being -30 , and is fairly constant, showing that French turpentine has a very uniform composition; this fact is also shown by its regular specific gravity and by its steady distillation temperature. The specific rotation of the pure terpene, terebenthene, is -40 . American turpentine rotates the ray to the right, but the variation of the value in different samples is very great; ordinary commercial samples give specific values ranging from $+8$ to $+16$; the pure terpene has a specific rotation of $+21.5$. It is quite possible that American turpentine contains a small quantity of a lævo-terpene, the quantity of which varies in amount and, consequently, the specific rotation must vary also. The air oxidation products (sobrerol) in their action on polarised light vary with the turpentine from which they are obtained; that from French turpentine rotates the ray to the left with a fairly uniform specific value, while that from American turpentine is rather variable and can be separated into two varieties, one with a $+$ and the other with a $-$ specific rotation; while, by mixing the two in equal proportions, an inactive variety can be obtained. Burmese turpentine from *Pinus Khasyana*, which resembles French and American turpentine in its general properties, differs by having a strong and uniform $+$ rotation.

Russian turpentine resembles American turpentine in many of its properties, such as solvent and soluble features, action of nitric acid, sulphuric acid, chlorine, &c. It is rather more

variable in composition and specific gravity, which latter varies from 0.862 to as high as 0.873. It begins to boil at about 156° C., but is not completely distilled below 180° C., the great bulk passing over between 172° and 174° C.; this greater range of distilling temperature points to a more complex composition than that of other turpentines. It has an odour resembling that of American turpentine, but differing slightly therefrom. It is rather more volatile. It rapidly absorbs oxygen from the atmosphere, becoming very viscid; partly on this account and partly on account of its stronger odour, Russian turpentine has not come so much into use in making paints. It is said to induce headache when being used; this phenomenon will depend a great deal on the physiological idiosyncrasies of particular individuals. The oxidation-product which is formed has, according to Kingzett, the composition $C_{10}H_{14}O_4$, and he has named it camphoric peroxide; on heating with water, this gives rise to the formation of camphoric acid, $C_{10}H_{16}O_4$, and hydrogen peroxide, H_2O_2 . On this property of Russian turpentine is based its use in the preparation of the disinfectant, "Sanitas."

Russian turpentine exerts a strong rotary action on polarised light, the specific value varying as much as from + 15 to + 23, while the pure terpene, sylvestrene, has a specific rotation of + 19, which shows that the commercial turpentine must contain terpenes of higher rotary power, the amount of which varies in different samples. In all other properties Russian turpentine resembles American turpentine.

Of late years a great many substitutes for turpentine have been placed on the market under a variety of fancy names, "patent turpentine," "turpentyne," "turpenteen," &c. These will be discussed later on (see p. 371).

Turpentine is frequently adulterated, the adulterants usually added being petroleum spirit, shale naphtha, rosin spirit, and coal-tar naphtha. The fact of the adulteration and the nature of the adulterant added is easily ascertainable, but the question of proportion of adulteration is a more difficult matter to ascertain, and demands the exercise of some considerable care and skill on the part of the analyst.

The property of acting on polarised light distinguishes turpentine from all bodies used to adulterate it; the specific value for each variety of turpentine has already been given; the presence of other bodies tends to reduce these values in proportion to the extent of the adulteration.

The specific gravity is a good indicator of adulteration, as, with the exception of coal-tar naphtha, the addition of other spirits tends to cause it to vary from the normal average of 0.867.

The addition of any of the adulterants named has a material influence on the temperature at which the turpentine begins to boil and those at which it distils. Genuine turpentine does not begin to distil below 150° to 156° C., the thermometer rising slowly from this point. In the case of French or American turpentines all is distilled over before the temperature attains 170° C., while with Russian turpentine the temperature may reach 180° C. before all is distilled. The greater portion of the turpentine passes over between 158° and 161° C. with American or French turpentines, while at least 93 to 95 per cent. passes over below 165° C. The great bulk of Russian turpentine passes over between 170° and 175° C. Adulterated turpentine begins to distil much below 150° C., in some cases below 80° C., according to the nature of the adulterant added; from the point at which the sample begins to distil there is a gradual increase of temperature; the thermometer rises slowly, and in some cases the distillation is not complete at 200° C. By comparing the temperature at which the sample distils with the distillation temperatures of the possible adulterants as given in the descriptions of these bodies some idea of the nature and the approximate amount added of the adulterant may be obtained.

The simplest method of ascertaining the distillation temperatures of turpentine is by means of a retort; this should have the capacity of 150 c.c. and be provided with a stopper. Through the tubulure is passed a thermometer; 100 c.c. of the turpentine is measured into the retort; the bulb of the thermometer is completely immersed in the liquid; while the beak of the retort is connected with a Liebig's condenser. A cylindrical measuring glass of 100 c.c. capacity serves as a receiver. Heat is applied to the retort, and the temperature at which the liquid enters into ebullition, and gives off vapour which condenses in the beak of the retort is noted; the rise of thermometer and the quantity of distillate collected in the receiver is also noted from time to time. The distillation need not be carried to complete dryness, but may be stopped when about 5 per cent. is left in the retort.

The distillation may be carried out in a fractionating flask, which is a flask fitted with a tube in the side of the neck, which tube is connected with a condenser. Into the mouth of the flask is fitted a thermometer, the bulb of which is arranged to be opposite the side tube. 100 c.c. of the sample is measured into the flask and the sample distilled as before. More uniform results can be obtained by using a fractionating flask than with a retort, the thermometer registering more accurately the temperature of the vapour as it passes to the condenser.

Petroleum or *shale naphtha* in turpentine may be detected by

the flash point, which in genuine turpentine is about 90° to 100° F., while the naphthas flash at 60° to 70° F.; the addition of 10 per cent. of these is sufficient to affect the flash point. A method of ascertaining the addition and the amount of these bodies can be based on the fact that while turpentine can be distilled in a current of steam, the shale and petroleum naphthas cannot. Into a retort is placed 100 c.c. of turpentine, which is gently heated by means of a Bunsen burner; through the retort is passed a current of steam generated by boiling water in a flask, the steam from which is passed through the turpentine in the retort. The distillation is carried on until no more spirit passes over, a Liebig's condenser being used to condense the vapours which pass over. Under these conditions genuine turpentine does not leave more than 0.2 per cent. of unvolatile residue if fresh; old samples may leave as much as 0.5 per cent. Any residue above 0.5 per cent. which may be left in the retort may be considered to be evidence of adulteration, and its nature can be ascertained by a few experiments. Those portions of the naphthas from either shale or petroleum which are volatile below 100° C. will pass over with the turpentine; in this event the distillate will have a specific gravity below 0.800, as a rule.

Rosin spirit is rather more difficult to detect when it is used for adulterating turpentine. It increases the specific gravity. Its wide range of distilling temperatures and its odour are sufficient to detect it, but there is no satisfactory method of determining the proportion which may have been added; the steam distillation process gives the best results.

Coal-tar naphtha is not much used for adulterating turpentine; it has much about the same specific gravity, flashes at about the same temperature, has a wider distilling range of temperature, is more volatile, and has a peculiar odour.

A table will be found on p. 379 giving, in a comparative form, a synopsis of the properties of turpentine and its adulterants, which will be found useful in making the analysis of an adulterated sample.

TURPENTINE SUBSTITUTES.—A number of these bodies are now offered to painters under various fancy names, (see p. 369). The composition of these bodies necessarily varies; some are simply heavy petroleum hydrocarbons of about 0.790 specific gravity and flashing at about 120° F. An example of such will be found on p. 376. Others are mixtures of turpentine, rosin spirit, and benzoline, in various proportions, while others contain only rosin spirit and petroleum light oils.

The properties of these bodies will be those of their various

is a point of distinction from turpentine, and points to complexity in the composition of rosin spirit.

Rosin spirit is insoluble in water and alcohol, but is soluble in ether, or a mixture of alcohol and ether, as also in turpentine, chloroform, and petroleum spirit. Nitric acid acts on it rather less energetically than on turpentine, forming with it a dark scarlet mixture; hydrochloric acid has but little action. Sulphuric acid forms a dark red mixture; probably there is some polymerisation.

In composition rosin spirit is a mixture of several hydrocarbons the exact nature of which has not yet been thoroughly worked out. From rosin spirit has been isolated heptene, C_7H_{12} , a colourless, limpid liquid, having a specific gravity of 0.8031, and boiling at 103° to 104° C.; on exposure to the air it absorbs oxygen. Sulphuric acid polymerises it with the formation of diheptene, $C_{14}H_{24}$, which boils at from 235° C. to 250° C., and which, on exposure to the air, rapidly absorbs oxygen and resinifies. Heptene exposed to air in the presence of water forms crystals having the formula $C_7H_{12}(OH)_2H_2O$. It combines with bromine to form the compound $C_7H_{12}Br_2$, which is a heavy yellow oil. In light rosin spirit, containing constituents boiling below 100° C., there have been found hexylene, C_6H_{12} , and amylenene, C_5H_{16} .

Rosin spirit is the best substitute for turpentine known, and is capable, when of good quality, of replacing it for all purposes. The chief objection to it lies almost entirely in its odour, which is not so pleasant as that of turpentine. Then, again, if sufficient care has not been taken in refining it, it is apt to contain traces of rosin oil, which would prevent it from drying properly. The specific gravity of a good sample of rosin spirit should not exceed 0.880, and all should distil below 250° C.; it may be taken for granted that any residue left at temperatures above 250° C. will consist chiefly of rosin oil, which reduces the value of the rosin spirit, owing to its want of drying properties. Rosin spirit is used in making some of the turpentine substitutes which are now so common.

The only possible adulterants for rosin spirit are shale naphtha and petroleum benzoline—the presence of which can be ascertained by the application of the tests for specific gravity, flash point, and distillation temperatures, as in the case of turpentine.

Rosin spirit is largely used in making cheap varnishes, using rosin (as the body), gum, and, occasionally, colouring the varnish with pigments.

SHALE SPIRIT or **SHALE NAPHTHA**.—When the shale found in the South of Scotland, in the district lying between Glasgow and Edinburgh, is distilled at a comparatively low temperature, there is given off a quantity of tarry matter known as “crude oil;” this is a product of very complex composition, which, on redistillation, gives a purer product known as “once-run oil.” This is further refined by treatment, first, with sulphuric acid (to remove basic impurities), and then with caustic soda (to remove acid impurities); finally, it is distilled, when it yields three chief products—“green naphtha,” “twice-run light oil,” and “green oil.” The two latter do not interest painters.

The “green naphtha” is refined by treatment with sulphuric acid, caustic soda, and redistilling, when there is obtained a very limpid, water-white liquid, known commercially as “naphtha” or “shale spirit”; the yield is about 5 per cent. of the crude oil.

Shale naphtha is a water-white, very limpid liquid, having a specific gravity of 0.730 to 0.760, and a slight odour. It is insoluble in water and alcohol, but mixes freely with ether, turpentine, benzol, &c.; while it readily dissolves all oils (except castor oil), some of the resins (such as gum dammar) in the natural state, and nearly all when they have been partially decomposed by fusion. It is very volatile, and, unlike either turpentine or rosin spirit, evaporates without leaving any residue behind.

It is inflammable, readily taking fire at ordinary temperatures, which is one objection to its use. It begins to boil below 100° C., and is generally completely distilled over below 190° C.; the range of temperature and the proportion which distils over varies with different makes. A sample (sp. gr., 0.760) tested by the author distilled as follows:—

First drop at	71° C.
3 per cent. came over below	90° C.
10	”	”	.	.	.	120° C.
23	”	”	.	.	.	143° C.
43	”	”	.	.	.	150° C.
60	”	”	.	.	.	160° C.
70	”	”	.	.	.	170° C.
81	”	”	.	.	.	180° C.
90	”	”	.	.	.	190° C.

A naphtha of 0.730 specific gravity will boil at lower temperatures than these.

Acids and caustic alkalis have no action on shale spirit. It absorbs a small quantity of bromine or iodine.

Shale naphtha is a complex mixture of hydrocarbons belonging to the two series, paraffins and olefines, the latter forming about 60 per cent. of the naphtha. There have been found hexene, C_6H_{12} ; heptene, C_7H_{14} ; octene, C_8H_{16} ; and nonene, C_9H_{18} among the olefines; hexane, C_6H_{14} ; heptane, C_7H_{16} ; octane, C_8H_{18} ; and nonane, C_9H_{20} among the paraffins; but other members of these two series are present.

Shale naphtha is largely used as a substitute for turpentine, and on the whole is a good material for the purpose. It is distinguished from both turpentine and rosin spirit by its much lower gravity, its flash point, its indefinite boiling point, the low temperatures at which it distils, by not being affected by sulphuric acid, and by not being completely distilled in a current of steam as is turpentine.

BENZOLINE, Benzine, or Petroleum Spirit.—When the petroleum obtained from the oil wells of North America is subjected to distillation three products are obtained—viz., “naphtha,” “kerosine,” and “residuum.”

The “naphtha” is refined by treating with sulphuric acid, then with caustic soda, and distilling, when three products are obtained—viz., “gasoline,” “benzoline,” and “naphtha.” The first—gasoline—is a very light product, having a specific gravity varying from 0.680 to 0.700, and is used only for special purposes. The other two products are sold indiscriminately under the names of “benzoline,” “benzine,” and “petroleum spirit.” These products vary much in quality. They are water-white, very limpid liquids having a specific gravity ranging from 0.730 to 0.760, but heavier samples are met with.

In its general properties benzoline resembles the shale naphthas; what is generally sold under that name has a specific gravity of about 0.730; it flashes and takes fire at the ordinary temperature; it begins to distil at about $65^{\circ}C.$, and is usually completely volatilised at $150^{\circ}C.$

A sample tested by the author gave the following results:—

First drop came over at	$65^{\circ}C.$
5 per cent.	„	below	.	.	.	$70^{\circ}C.$
14	„	„	„	.	.	$75^{\circ}C.$
22	„	„	„	.	.	$80^{\circ}C.$
31	„	„	„	.	.	$85^{\circ}C.$
46	„	„	„	.	.	$90^{\circ}C.$
58	„	„	„	.	.	$95^{\circ}C.$
64	„	„	„	.	.	$100^{\circ}C.$
70	„	„	„	.	.	$105^{\circ}C.$
80	„	„	„	.	.	$110^{\circ}C.$
90	„	„	„	.	.	$120^{\circ}C.$

This is a light sample; usually only about 50 per cent. distils over below 100° C.; and some samples do not contain any portion distilling below 100° C.

In its general features, chemical composition, and uses, petroleum spirit resembles shale spirit; it contains, however, a larger proportion of the paraffin hydrocarbons.

Certain substances are met with in the market, and sold as "turpentine substitute," and other fancy names more or less resembling turpentine, which are petroleum and paraffin products rather heavier than naphtha. A sample of such examined by the author had a specific gravity of 0.7913, a flash point of 36° C. (97° F.), and began to distil at 156° C., the rate of distillation being as follows:—

25 per cent. below	180° C.
50	"	"	200° C.
70	"	"	210° C.
76	"	"	215° C.

No further portion was distilled.

Such products are rather slow in drying, but they are better substitutes than petroleum spirit, because they are less inflammable, and there is, therefore, less risk of fire in using them. They do not oxidise or leave any residue on evaporation.

COAL-TAR NAPHTHA.—Coal-tar naphtha is not much used in paint-making; but in the preparation of varnishes it finds some use. It is one of the products obtained during the distillation of coal-tar. In this operation several products are obtained, the proportion and nature of which depends partly upon the composition of the tar and partly upon the manner in which it is distilled. Among the products is a light oil or spirit of a dark brown colour, known as "naphtha" or "light oil;" in specific gravity it ranges from 0.840 to 0.940. Its odour is characteristic, but somewhat disagreeable. Its composition is complex, containing hydrocarbons of the paraffin and olefine series in small quantities, but its characteristic constituents are hydrocarbons of the benzene series, such as benzene, C_6H_6 ; toluene, C_7H_8 ; xylene, C_8H_{10} ; cumene, C_9H_{12} ; durene, $C_{10}H_{14}$; besides these it contains ammonia, aniline, toluidine, and other nitrogenous bodies; alcohol, phenol, acetic acid, and sulphur compounds.

It is purified by re-distillation, when what is called "once run naphtha" is obtained; this is further purified by treatment with sulphuric acid, which removes all the basic bodies, the hydrocarbons of the olefine and crotonylene series, and the higher members of the benzene series. After separating the acid from

the semi-purified naphtha, the latter is treated with caustic lime or caustic soda, which removes all the oxygen and sulphur compounds; finally, the naphtha is well washed with water, and is then ready to be finally purified by a re-distillation.

Once run naphtha has a specific gravity of 0.886 to 0.893, and is the raw material for the preparation of 90 per cent. benzol, "50/90 per cent. benzol," 30 per cent. benzol, solvent naphtha, and burning naphtha, as the commercial products are named.

The benzols are light products used in the manufacture of aniline dyes. Burning naphtha, which has a specific gravity of about 0.880 to 0.887, is sold for burning in out-door lamps, especially costermongers' lamps, although it has of late been largely displaced by the petroleum oils for this purpose.

Solvent or coal-tar naphtha is largely used in the india-rubber industry, and for making varnish. It is a water-white liquid, having a peculiar and characteristic odour of coal-tar hydrocarbons; in specific gravity it varies somewhat, the usual range being between 0.865 to 0.877. On being subjected to distillation, it gives from 8 to 30 per cent. of distillate below 130° C., while as a rule 90 per cent. distils over below 160° C. It burns with a very smoky flame, and is very inflammable, the flash point being about 120° F. It is miscible with alcohol, ether, turpentine, petroleum spirit, shale naphtha, and other similar solvents, while it is a good solvent for oils, fats, resins, and is almost the only solvent for coal-tar pitch, and other pitches.

In composition it is very complex, but it consists chiefly of the three isomeric, para-, meta-, and ortho-xylenes, C_8H_{10} , cumenes, small quantities of paraffins and olefines, and occasionally traces of naphthalene. Sulphuric acid has little or no action on coal-tar naphtha, but nitric acid has a powerful action, and transforms the coal-tar hydrocarbons into the nitro derivatives, nitroxylenes, $C_8H_9NO_2$; nitro-cumenes, &c. Hydrochloric acid, caustic soda, and caustic potash have no action on it.

It is used in making cheap quick-drying varnishes, rosin being the usual substance added to give the requisite coat; it is more volatile than turpentine, although it does not leave any residue behind it.

Commercial coal-tar naphtha is occasionally adulterated with petroleum or shale spirit, or with petroleum or paraffin burning oils; in every case the specific gravity and flash points are reduced. The addition of the petroleum and shale spirits causes it to distil at lower temperatures and a little more regularly, while the burning oils raise the distillation temperatures rather considerably.

Such additions may also be detected by treating the suspected sample with a well-cooled mixture of sulphuric and nitric acids, which converts all the coal-tar hydrocarbons into nitro-compounds, while the paraffin or petroleum oils are unaffected; if now water is added, the nitro bodies, being heavy, sink to the bottom, while the petroleum hydrocarbons being light rise to the top, and may be collected and measured. It should be pointed out that finding a small amount of such unchanged hydrocarbons does not necessarily indicate adulteration, as coal-tar naphtha naturally contains small quantities of paraffin hydrocarbons.

The best method of examining coal-tar naphtha for its quality is by distillation. The method commonly used is the following:—100 cc. of the naphtha is measured by means of an accurate glass measure into a tubulated retort of 200 cc. capacity; through the tubulure is inserted a thermometer, the bulb of which reaches within $\frac{3}{8}$ of an inch of the bottom of the retort. The beak of the retort is connected with a long Liebig's condenser, and the distillation carried on by means of a Bunsen burner. It is best to insert the bulb of the retort into a deep sand bath, so that if the retort should crack, the naphtha would flow into and be absorbed by the sand, and no disastrous results ensue. The temperature at which the first drop flows from the end of the condenser is noted; with naphtha this occurs at about 110° C. Then the rate of distillation is noted; at 120° C. about 20 per cent. will come over, at 130° C. about 60 per cent., at 140° C. about 72 per cent., and 90 per cent. usually comes over below 150° C. Or, instead of taking the temperatures, as in the above example, and noting the quantity distilled at them, the temperature at which each successive 10 cc., or 10 per cent., comes over may be noted; the results will then be somewhat as follows:—10 per cent. at about 128° C., 20 per cent. at 130° C., 30 per cent. at 132° C., 40 per cent. at 135° C., 50 per cent. at 137° C., 60 per cent. at 140° C., 70 per cent. at 145° C., 80 per cent. at 148° C., 90 per cent. at 158° C. Addition of petroleum or shale spirits increases the proportion distilled at the different temperatures, while petroleum or paraffin burning oils decreases the proportion considerably. Sometimes the makers take out the lower benzene hydrocarbons and thus reduce the value of the coal-tar naphtha for the particular purpose; in such case, the temperature of distillation will be increased.

The following table shows, in a comparative form, the properties of turpentine, rosin spirit, shale and petroleum spirits, and coal-tar naphtha:—

	Turpentine.	Rosin Spirit.	Shale and Petroleum Spirits.	Coal-tar Naphtha.
Smell, cold, .	Peculiar.	Turpentinous.	None or slight.	{ Smell of coal-tar.
„ on warm- ing, . }	„	Of rosin.	Slight.	
Taste, . . .	Characteristic	{ Peculiar after-taste.	Variable and slight.	{ Strong.
Specific gravity,				
Fluorescence, .	None.	Slight.	Slight.	None.
Rotary power,	Strong.	„	None.	„
Sulphuric acid {	Slight; poly- merises on heating. }	„	Slight.	Slight.
Nitric acid, . .				
Boiling point, .	156° C.	{ High and variable.	Low and variable.	High and variable.
Flash point, {	36° C.	37° C.	Ordinary temperature.	40° C.
	97° F.	98°·5 F.		

METHYLATED SPIRIT—Methylated spirit is a very useful article in the preparation of varnishes and enamel paints. It consists essentially of a mixture of two bodies, methyl alcohol and ethyl alcohol; but in the ordinary commercial qualities there are usually small traces of other bodies, some of an ethereal character, others of an acid character.

The alcohols are a very large and important group of chemical compounds, many of them finding extensive application in the various chemical arts. The type of the group is ethyl alcohol, C_2H_5OH , the body usually understood by the term alcohol when used by itself. It is also known as spirit of wine, for to it is due the intoxicating effect of wines, spirits, beers, and all beverages which have undergone fermentation.

Pure ethyl alcohol is a colourless, very limpid liquid, having a pleasant odour and a hot burning taste. It is very volatile when exposed to the air, passing off completely and leaving no residue behind. It boils at 78°·5 C. (173° F.) and distils over completely and unchanged at that temperature. It is only solidified when subjected to the very low temperature of -130° C. The specific gravity of pure alcohol at 15°·5 C. (60° F.) is 0·7935; but it has such an affinity for water that the preparation of a sample absolutely free from water is exceedingly difficult, so that the gravity given above may not be quite correct, but the error, if there is any, is small. Alcohol mixes with water in all proportions; if the two bodies are fairly pure the proportion of alcohol

may be ascertained by simply determining the specific gravity (see table on p. 382). It mixes with ether, chloroform, turpentine, carbon bisulphide, and benzol, but not with petroleum products. It dissolves fatty acids and castor oil readily, but it has only a slight solvent action on the other fatty oils. It dissolves rosin and a few other resins, such as, shellac, sandarac, mastic, more or less completely; but it will not dissolve the hard copals, animi and kauri. It is a powerful solvent for coal-tar dyes, and other bodies.

When subjected to the action of oxidising agents it is first transformed into aldehyde, $\text{C}_2\text{H}_3\text{COH}$, and then, finally, into acetic acid, $\text{C}_2\text{H}_3\text{COOH}$.

It is obtained as a product of the fermentation of sugar; this body, which is present in grapes, malt, and fruits of all kinds, if kept under conditions which cause it to enter into fermentation, loses carbonic acid and water, while alcohol is formed in fair proportions; this passes into the water in which the process is conducted and from which it is separated by distillation, and redistillation with the aid of quicklime.

The alcohol ordinarily met with in commerce is known as "rectified spirit of wine;" this has a specific gravity of 0.838, and contains 86 per cent. of real alcohol; what is known as "proof spirit" has a specific gravity of 0.926, and contains 49 per cent. of real alcohol.

Alcohol alone is not used in the preparation of varnishes as the high rate of duty levied by the Excise Authorities prohibits its use for this purpose.

Methyl alcohol is a homologue of ethyl alcohol; and has the composition indicated by the formula $\text{C}_2\text{H}_5\text{OH}$. When pure it is a colourless liquid, very mobile and volatile, which has a fragrant spirituous odour, and boils at 55°C . Its specific gravity at $15^\circ.5\text{C}$. (60°F .) is 0.8021, but authorities vary a little on this point. It is miscible in all proportions with water, from which it is not easily separated; it also mixes freely with alcohol, ether, turpentine, &c., and possesses great solvent properties for resins, &c.

When subjected to the action of oxidising agents it is first changed into formaldehyde, HCOH , then into formic acid, HCOOH .

Methyl alcohol is obtained in large quantity in the dry distillation of wood. The wood is placed in iron stills or retorts in suitable furnaces, when there come over gaseous vapours, which condense, partly into an aqueous layer, and partly into a tarry mass. The aqueous layer, which has an exceedingly complex composition, contains acid, alcoholic, phenolic, ethereal and

other compounds. It is separated from the tar, treated with slaked lime, and then subjected to heat; crude wood-spirit distils over, while impure acetate of lime is left behind in the still.

The spirit is very impure, and is further treated by redistilling for quicklime, then treating with sulphuric acid (which removes ammonia and methylamine) and, finally, redistilled with lime.

Crude wood-spirit, as obtained by the above process, is a liquid of complex composition, containing about 95 per cent. of methyl alcohol in the best qualities, although some samples do not contain more than 40 or 50 per cent. The following bodies are found in wood-spirit, or wood-naphtha as it is sometimes called:—Methyl alcohol, $\text{C H}_3 \text{ O H}$; acetone $(\text{C H}_3)_2 \text{ C O}$, sp. gr. 0.792, b. p. $56^\circ\cdot5 \text{ C.}$; allyl alcohol, $\text{C}_3 \text{ H}_5 \text{ O H}$, sp. gr. 0.8604, b. p. $96^\circ\cdot5 \text{ C.}$; furfurol, ketones, &c.

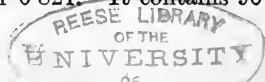
The odour of wood-naphtha is characteristic and somewhat unpleasant. It is due entirely to the impurities which are present in the spirit. Its taste, for the same reason, is extremely nauseous; hence the use of wood-naphtha in making methylated spirit.

Wood-naphtha is used for dissolving gums and resins in varnish making, and it is worth noting that many of the gums are more freely soluble in the crude wood-naphtha than they are in the pure methyl alcohol. The cause of this increased solvent power of the crude spirit must reside in the ethereal impurities it contains, many of which dissolve resins more freely than does methyl alcohol.

The following reactions serve to distinguish wood-spirit from pure methyl alcohol:—caustic soda gives a brown colour, sulphuric acid a red colour, which increases in depth on heating; mercurous nitrate gives a grey precipitate of mercury.

Methylated spirit is a mixture of 90 parts of rectified spirit of wine with 10 parts of wood-spirit, and this mixture is permitted by the Excise authorities to be sold, under special regulations, for manufacturing purposes free of duty, the addition of the wood-spirit rendering the spirit undrinkable. Of late, however, owing to improvements in the manufacture of the wood-naphtha, much of the nauseous taste is removed, and the methylated spirit now made is not so undrinkable. On this account the Excise authorities have recently compelled the addition of $\frac{1}{2}$ per cent. of petroleum oil to the methylated spirit, with the object of rendering it still more undrinkable, but the use of the original spirit is still by special permit allowed.

The methylated spirit is usually sold at a strength of "64 over proof," and has a specific gravity of 0.821. It contains 90 per



cent. of real alcohol. The meaning of the term "64 over proof" is that when 100 volumes of this spirit is mixed with 64 volumes of water, there is obtained "proof spirit," which is a spirit of such a strength that when mixed with gunpowder it will not set fire to the powder when a light is put to it. The term "proof spirit" is very vague, and should be done away with. It would be better to sell the spirit according to the actual quantity of alcohol it contains.

The strength of methylated spirit may be fairly accurately estimated from its specific gravity. Tables have been constructed showing the quantity of alcohol contained in spirit of different gravities. Space cannot be spared in this book for the reproduction of those tables, but the following table contains some information on this point which may be of use:—

Sp. Gr. at 60° F.	Per Cent. of Alcohol.	Per Cent. of Proof Spirit.	Sp. Gr. at 60° F.	Per Cent. of Alcohol.	Per Cent. of Proof Spirit.
0·79384	100	175·25	0·880	66·7	129·5
0·800	98	173	0·890	62·3	122·5
0·810	94·6	169·2	0·900	58·0	115·3
0·820	91	164·75	0·910	53·57	107·6
0·830	87·2	159·75	0·91984†	49·24	100
0·8382*	84	155·45	0·920	49·16	99·8
0·840	83·3	154·5	0·930	46·64	91·64
0·850	79·3	148·8	0·945	39·8	85·59
0·860	75·1	142·6	0·950	34·5	82
0·870	70·84	136			

* Rectified spirit of wine.

† Proof spirit.

Methylated spirit generally has an acid reaction, due to the presence of small quantities of acetic acid and aldehyde; besides these, it contains traces of higher alcohols (amyl alcohol, propyl alcohol), oily and resinous bodies, ethereal compounds, and water.

Methylated spirit is used in making varnishes from shellac, sandarac, rosin, mastic, dammar, and other resins; such varnishes are very quick in drying owing to the volatility of the methylated spirit. It is also used in the preparation of enamel paints.

The quality of methylated spirit may be ascertained by distilling 100 c.c., when nearly all should be distilled below 100° C., the great bulk passing over between 80° and 90° C. The specific gravity is also a good indication of the quality, as shown in the table given above. In making any determination of the specific

gravity particular attention must be paid to the temperature at which it is determined, as small variations of temperature cause considerable alteration in the gravity; the standard temperature is $15^{\circ}5$ C. (60° F.). The actual determination may be made by means of an hydrometer—either the glass one; or the metal one, known as Sikes' hydrometer, which is used by the Excise authorities; or the specific gravity bottle may be used.

Finish or methylated finish is methylated spirit containing about 3 oz. of rosin to the gallon. For some purposes this may be used in the place of methylated spirit, as the Excise do not place so many restrictions on its sale. It may be distinguished from the pure spirit by its giving a very copious white precipitate when water is added to it.

On the Continent distilled animal or "Dippels" oil is used for the denaturing (or rendering undrinkable) of alcohol; the use of this material has not been adopted in this country.

CHAPTER XIII.

D R I E R S .

DRIERS are a class of bodies added to oil for the purpose of causing it to dry quicker than it would otherwise do. The bodies generally used for this purpose are salts of iron, lead, manganese, and zinc. The following list comprises all the compounds used as driers in paints and varnishes:—Red lead, litharge, lead acetate, lead borate, manganese oxide, manganese sulphate, manganese borate, manganese oxalate, zinc oxide, zinc sulphate, and ferrous sulphate.

Of these, the lead salts are most in use; the manganese compounds are largely used; the others but rarely.

Red Lead is fully described on p. 93, *et seq.*

Litharge is the monoxide of lead, and has the composition shown by the formula PbO . It is prepared by oxidising lead in a current of air at a temperature sufficiently high to melt the oxide as it forms. On cooling, the litharge separates out in the form of flakes of a red-brown colour, which, on being ground up, forms a buff-coloured powder. Litharge is sold in the two forms here noted. It is soluble in dilute nitric acid and in acetic acid, forming the corresponding nitrate or acetate of lead. Hydrochloric acid dissolves it on boiling, forming the chloride; while sulphuric acid does not dissolve it, but forms the insoluble sulphate of lead. Mixed with oils, a slow action sets in, resulting in the formation of lead soaps, which are insoluble in water and many solvents. This action occurs with linseed oil; the lead linoleate so formed dissolves in the rest of the oil, forming a kind of varnish, which, on drying, leaves a lustrous coat. It is this feature of lead salts that makes them valuable in the production of paint. Litharge is a powerful drier, and should not be used too extravagantly in the boiling of oil; about $\frac{1}{2}$ lb. to the cwt. of oil is quite sufficient.

Red lead is also a good drier, even better than litharge, from $\frac{3}{4}$ lb. to 1 lb. being sufficient for 2 cwts. of oil. Its action on oil partakes more of the nature of an oxidising action than does

that of litharge, while it is dissolved in the oil in the nature of a lead soap, as is the case with litharge. Both litharge and red lead are largely used in the preparation of boiled oil. The oil so prepared has a dark red colour, but dries quickly, and leaves a coat which is elastic and yet firm to the touch, so that it is capable of resisting a great deal of rough wear and tear, as also exposure to considerable variations of temperature.

Lead acetate, $\text{Pb } 2 \text{ C}_2 \text{ H}_3 \text{ O}_2$, is a white crystalline solid prepared by dissolving lead or litharge in acetic acid, and evaporating the solution down to dryness, or until it crystallises. It is readily soluble in water, and to a small extent in alcohol. It is used as a drier, principally for mixing with paints, and then it gives good results. Paint to which lead acetate, or sugar of lead as it is called, is added dries better on greasy surfaces than paint to which nothing has been added. As a drier it is not equal to either red lead or litharge, but it has the advantage of not causing the oil or paint to become dark or coloured. It is used in making what are called patent driers.

Lead borate is a white powder prepared by adding a solution of borax to one of lead acetate or nitrate. The precipitate is collected, washed, and dried. It is largely used as a drier both in boiling oil and in mixed paints. It does not lead to the discolouration of the oil so much as red lead, while its drying properties are nearly equal to those of litharge. From $\frac{3}{4}$ lb. to 1 lb. is sufficient for 2 cwts. of oil or paint.

Manganese dioxide, the black oxide of manganese, Mn O_2 , is now very extensively used as a drier. It comes into the market from two sources, one natural, the other artificial. The natural manganese forms the mineral manganese or pyrolusite, and is found widely distributed in large quantities; for use, it is simply ground to a powder with water and then dried. It forms a greyish-black powder insoluble in water. Artificially, manganese is obtained from the still liquors of the bleaching-powder manufacturer, who, to prepare chlorine, treats manganese with hydrochloric acid, when he obtains a solution of manganese chloride, Mn Cl_2 ; this is treated by a process invented by Weldon, when all the manganese it contains is recovered in a usable form. While much of this recovered manganese is used over again in the preparation of chlorine, some of it is sold for other purposes. Manganese dioxide is soluble in hydrochloric acid with evolution of chlorine and the formation of manganese chloride, Mn Cl_2 ; in sulphuric acid it dissolves with evolution of oxygen and the formation of manganese sulphate, Mn S O_4 . Essentially it is a peroxide, a class of bodies which may be

described as containing more oxygen than is exactly equivalent to the metal present in them; this extra oxygen is often rather loosely combined, and ready to enter into combination with other bodies; it is this feature in the composition of manganese which makes it useful in oil boiling, for the oxygen, during the process, combines with the oil and oxidises it, while the manganese dissolves to some extent in the oil in the form of a manganese compound of the linoleic acid of the oil. Manganese is in consequence a powerful drier; in fact, the most powerful known. The proportion usually added in the process of boiling is $\frac{1}{4}$ lb. to 1 cwt. of oil, and it is not desirable to increase this proportion much, as this would give rise to too much drying action, and cause the oil to form a hard and rather friable coat, not a firm elastic coat as it should do. Unfortunately, manganese has a tendency to make the oil dark. It is not a good drier for mixed paint, chiefly because the tendency in using it would be to add too much.

Manganese sulphate, $MnSO_4$, is prepared by dissolving manganese in sulphuric acid, and evaporating the solution down to dryness. It is a crystalline salt of a faint pink colour and somewhat hygroscopic properties; hence, it should always be dried before using as a drier. Its drying action is, perhaps, rather more powerful than that of the lead compounds, but less than that of the last-named compound. Rather less than $\frac{1}{2}$ lb. should be added to each cwt. of oil or paint. It possesses one advantage over manganese in not adding to the colour of the oil. Owing, however, to its somewhat hygroscopic properties it is not largely used as a drier.

Manganese borate is a powder of a faint pinkish hue prepared by adding a solution of borax to one of a manganese salt, such as the sulphate or acetate; the powder is collected, washed, and dried, when it is ready for use. As a drier it is one of the best and most powerful, being superior to the lead compounds, but inferior to manganese, although it has the advantage of not leading to any discolouration of the oil. Between $\frac{1}{4}$ and $\frac{1}{2}$ lb. is required for each cwt. of oil.

The use of manganese linoleate, prepared by adding a solution of linseed oil soap to one of manganese chloride, has been lately proposed and patented. By using this product in a special way "boiled" oils are obtained much heavier than ordinary boiled oil, yet paler in colour.

Manganese oxalate, MnC_2O_4 , has lately been proposed to be used as a drier for oil, and is said to have some advantages over other manganese compounds. It is prepared by precipitating

manganese salts with oxalate of potash or soda; or by treating manganese hydroxide with oxalic acid. One advantage is said to be that during the process of oil-boiling it is decomposed, and that, owing to the manganese dissolving in the oil in combination with the linoleic acid and to the oxalic acid being evolved in the form of carbonic acid, the metal is able to exert its greatest drying power. From $\frac{1}{4}$ to $\frac{1}{2}$ lb. may be used per cwt. of oil.

Zinc oxide, Zn O , is used as a drier, but cannot act as such as it has no drying properties at all. It is often put in mixed driers (see below), where it acts as a diluent to decrease the drying power of the other ingredients. For a description of its properties see p. 58.

Zinc sulphate, Zn S O_4 , is also used as a drier, but its virtues in this respect are rather problematical. As the commercial product contains much water of crystallisation it is necessary to dry it before it is added to the oil.

Ferrous sulphate, copperas, Fe S O_4 , is frequently added as a drier, especially in the preparation of varnishes. It is in the form of pale bluish-green crystals, containing 5 molecules of water of crystallisation; hence, before being used, it must be dried to dehydrate it. It is soluble in water. It is prone to decomposition by oxidation, especially if the crystals be exposed to moist air; it is this property of being changed by oxidation from ferrous sulphate to ferric oxide that makes copperas useful as a drier. It should be used with care, as its tendency is to harden the coat of paint or varnish, and thus impart a tendency to crack. It is not by any means such a good drier as either lead or manganese salts; from 1 to 2 lbs. are required for 1 cwt. of oil.

Besides the simple driers described above, a variety of compound driers, usually composed of mixtures of the single driers in various proportions or with some linseed oil or boiled oil, are made; it is not intended to describe these in detail, but a few recipes for the production of those principally in use will be given.

Patent Driers.—Take 15 lbs. of dried zinc sulphate, 4 lbs. of lead acetate, and 7 lbs. of litharge; mix them with 4 lbs. of boiled oil, and grind well together. Mix 100 lbs. of Paris white and 50 lbs. of white lead with 30 lbs. of boiled oil, grind, and then mix with the first mixture, adding sufficient boiled oil to give the mass the consistency of soft dough.

The composition of the commercial "patent driers" varies with different makers, but the above is a common form.

Zumatic Drier.—25 lbs. of zinc white and 1 lb. of borate of manganese are ground together. The object of the zinc white is

simply to dilute the manganese salt, and to form a powerful drier in a convenient form. The proportions generally used are 1 lb. of the drier to 25 lbs. of paint.

Zinc Drier.— $6\frac{1}{2}$ lbs. of dry manganese sulphate, $6\frac{1}{2}$ lbs. of dry manganese acetate, $6\frac{1}{2}$ lbs. of dry zinc sulphate, and 980 lbs. of zinc white are ground together. From 2 to 3 per cent. of this is usually added to the paint. This is called zinc drier, because it was brought out as a drier for zinc white. It is also known as Guynemer's drier.

In both the above mixtures the manganese salts only act as driers; the other materials are really diluents, and of themselves can exert no drying action.

Oxidised Oil Driers.—Oxidised oil or well boiled linseed oil makes a good drier, very useful in many cases.

CHAPTER XV.

VARNISHES.

VARNISHES form a very important group of the materials used by the painter in carrying on his art. They are liquid bodies, more or less coloured, although colour is not an essential feature. When applied to the surface of a body, they lose a portion of their constituents by evaporation, and there is left a coat of a highly lustrous and durable character, thereby increasing the lustre of the object, developing its beauty, and protecting it from the destructive action of the atmosphere.

When varnishes were first introduced is very uncertain, but the kinds now in use are of modern origin, and mostly of English introduction, English varnishes being superior to those of any other country. Their use has, during the present century, increased very considerably, and has now attained very large proportions.

The subject divides itself into two parts—

- 1st, Varnish materials.
- 2nd, Varnish making.

1st, VARNISH MATERIALS.

The materials used in the manufacture of varnishes can be divided into six groups:—

- 1st, Drying oils.
- 2nd, Resins. (
- 3rd, Gums.)
- 4th, Solvents.
- 5th, Driers.
- 6th, Colouring matters.

In the trade, the second and third groups are generally classed together under one head—"gums."

✓ 1st, **DRYING OILS.**—These have already been considered (see p. 335, *et seq.*), and very little requires to be added here.

Linseed oil only has as yet been used in the preparation of oil varnishes, although some of the other drying oils could be used; but it is very doubtful whether they will give such good quality of varnish as linseed oil, and they are more costly, which is an important item in varnish making. The linseed oil used for making varnish should be of the very best quality—the best Baltic; other varieties of linseed oil only yield poor qualities of varnish. It should be kept at least twelve months before being used. It is best stored in old steam boilers, and it is essential that the air should be excluded. Nothing is definitely known as to the character of the action that goes on in the oil during the time it is thus stored; but there is a wonderful difference between unstored and stored oil in their varnish-making properties, the latter giving much the better results.

2nd, RESINS.—This is by far the most important group of varnish materials, for on these bodies the lustre and lasting properties of the varnishes depend. They are all of natural origin, being exudations from various species of trees.* They are very numerous. Some are used almost exclusively for varnish making, others are also used for other purposes, while some resins are not used for varnish making, but find use in other directions.

As a class, they are distinguished by being more or less hard, friable or brittle, lustrous, generally clear and transparent, although some are slightly opaque, insoluble in water, and soluble in alcohol, ether, benzol, and other solvents of a similar character, to a greater or less extent. In composition, they are very complex, being mixtures of bodies having acid properties. A few only of these bodies have been isolated and their characters definitely ascertained. In their ultimate composition they are rich in carbon, poor in oxygen, and contain no nitrogen. They are more or less combustible, usually burning with a smoky flame. They are usually devoid of colour, which is a valuable feature for varnish making, although some are coloured. As a rule, they are free from odour, but some possess fragrant and characteristic odours.

* All exudations from trees which form hard, more or less brittle masses, are termed in the produce markets and trade generally "gums"—*e.g.*, gum arabic, gum tragacanth, gum copal, gum animi, gum sandarac, &c., no matter what their origin or properties. True gums are those which are soluble to a greater or less extent in water (see p. 414), and resins are bodies which are not soluble in water, but soluble only in solvents like alcohol, turpentine, &c. In the following pages the word "gum" will (except as a trade description) be used exclusively for gums proper, and "resin" for the true resins, of which copal and animi are examples.

Classification of Resins.—The resins can be classed into various groups. Cooke classes them into three divisions:—1st, Resins; 2nd, Gum-resins; 3rd, Oleo-resins. The resins possess the properties enumerated above, and will be again referred to below. The gum-resins contain a little gum as well as resin in their composition; very few are used for varnish making. The oleo-resins consist essentially of a mixture of resin with a liquid oil which imparts to them a viscid character; they are useful bodies, although few find their way into varnishes. The resins can be divided into two groups—hard or copalline, soft or elemi resins; another method of grouping them is into oil-varnish resins, ethereal-varnish resins, and spirit-varnish resins. This latter classification will be adopted in this book as being of a practical nature.

Characters of Resins.—Some of these have been pointed out above in a general manner, but it is advisable to deal with them in a more detailed manner. The characters of resins which are of the most importance are form, appearance, colour, hardness, specific gravity, solubility.

Form.—Most resins occur in the form of knotty masses, some in the form of drops, and others in that of cylindrical pieces. The resin flows out of the tree in the form of drops; if the resin solidifies quickly it keeps this form, as, for example, mastic; if the process of solidification is slow, then the resin tends to form into tears or cylindrical pieces, as, for example, sandarac; if, again, the process goes on slower and the resin collects on the tree or drops on to the ground, it forms into knotty masses of various sizes and shapes, as, for example, copal, animi, dammar, &c. Some resins come into the market artificially shaped, as, for instance, gamboge in cylinders, shellac in thin plates, dragon's blood in thin sticks or powder, benzoin and elemi in blocks.

Appearance.—The appearance of many of the resins is characteristic. Animi is clear and transparent, and has a peculiar rough surface which, from its appearance, is known as the goose skin. Benzoin, elemi, and some others have more or less an agglomerate appearance, as if made up of two or three kinds of gum; such a structure is called by mineralogists *amygdaloidal*. Animi and copal have a very lustrous appearance; elemi, benzoin, &c., are more waxy; kauri partakes somewhat of both, and has a semi-lustrous appearance. Some—animi, copal, sandarac, dammar, and kauri—are more or less crystalline; while elemi and benzoin are amorphous in appearance. These points will be dealt with in detail when describing the resins individually.

✓ *Colour.*—Resins vary very much in colour. Accroides or xanthorrea is deep yellow, copal mostly of a pale straw, animi is a shade deeper, amber is of a brownish-yellow, and dragon's blood of a red colour; dammar is almost colourless; shellac has an orange colour; elemi is usually of a greyish tint, ammoniacum of a brown, and asphaltum a deep brown, almost approaching a black; the large majority of the resins are of a pale brownish colour. The colour of resins is a most important feature in varnish making, inasmuch as any colour they may possess affects the colour of the varnish made from them; the difference between two varnishes sometimes arises from the quality of the resin used, not in the kind of resin or other materials, nor in the method of preparation. In the best varnish the resin used is of the best quality, and has the purest colour; while inferior varnish is made with an inferior quality of resin, the colour of which is rather darker. In copal varnishes, for instance, where there are so many varieties of copal, so far as regards colour (ranging from almost colourless to pale brown), the palest copals only are used for pale copal varnishes, the oak varnishes being made from the darker coloured copals.

✓ *Hardness and Fusibility.*—In these two features, hardness and fusibility, there is a wide range of difference between the various resins. Some, such as the hard copals, amber, animi, are very hard and difficult to melt; these resins are the very best of the varnish resins, giving the finest and most durable kinds of varnishes, which are, however, the most difficult to make. Some resins, such as elemi, are so soft as to easily bend between the fingers, and will melt or become softened by the heat of the hands; such resins do not give durable varnishes, and they are only used to tone down the hardness and brittleness of other resins. Other resins, as animi and amber, are hard and difficult to break up; others again, as accroides, rosin, &c., are brittle and easily reduced to a powder; the former class yield durable varnishes, which, when applied to a surface, will stand a good deal of wear and tear; the latter class make varnishes which do not stand much wear and tear. The resins vary in the appearance of the fracture when broken; some exhibit a conchoidal or shell-like fracture, others a ragged appearance; some a powdery fracture, some a smooth fracture. The particular kind of fracture of each resin will be described when each resin is described in detail.

Specific Gravity.—Resins are all heavier than water; some, as copal, amber, and sandarac, are only slightly heavier; others, as benzoin, guaiacum, shellac, much heavier; the specific gravity of

each particular resin does not vary very much, so that this is a distinguishing feature which may be taken advantage of in making an examination of resins. The following table gives the specific gravity of most of the varnish resins :—

Animi, 1·043 to 1·067.	Thus, 1·042.
Amber, 1·074 to 1·094.	Dragon's blood, 1·200.
Benzoin, Siam, 1·235.	Elemi, 1·019.
„ Penang, 1·145 to 1·155.	Gamboge, 1·025.
„ Borneo, 1·165 to 1·170.	Guaiacum, 1·236 to 1·237.
Copal, Sierra Leone, 1·054.	Kauri, 1·050.
„ Angola, 1·064.	Mastic, 1·056 to 1·06.
„ Pebble, 1·055.	Sandarac, 1·038 to 1·044.
„ Manila, 1·063.	Shellac, 1·113 to 1·214.
Dammar, 1·055 (Batavian).	Accroides, 1·197.
„ 1·062 to 1·123	Locust, British Guiana, 1·030.
(Singapore).	Rosin, 1·044 to 1·100.

Solubility.—This is a very important property of resins, and influences to a very great extent the use to which they are put. There is a great deal of difference between the resins in regard to their solubility in various media; some, as animi and copal, are insoluble in any solvent, and before they can be made into varnishes have to be fused by heat; others, as shellac, sandarac, Manila copal, and rosin, are soluble in alcohol, ether, benzol, and are easily made into varnishes; other resins are not so easily soluble, such as dammar, mastic, &c. Acetone, ether, and benzol are the best solvents for resins; they will act more or less on all the resins of the last two classes. Petroleum spirit is a poor solvent for the resins, only rosin and dammar being dissolved by it.

OIL-VARNISH RESINS.—This class of resins includes—

Amber.	Sandarac.
Animi.	Rosin.
Copals.	Kauri.

As a class these resins are distinguished by being insoluble in oils, ether, and other solvents until after they have been more or less liquefied by fusion. There are one or two exceptions to this general statement; resin is soluble in alcohol as are also some of the soft copals and sandarac; but, otherwise, it holds good.

Amber.—This resin yields the finest and most durable varnish; its cost, however, prevents it from being very largely used for this purpose. Amber is a fossil resin found in the greensand beds of the Cretaceous period, in a narrow belt of districts extending from England through Holland, the Baltic

coasts of Germany, Russia, South Siberia, to North America; the quantity found in this country is unimportant, the great bulk of the supply coming from the Baltic coasts of East Prussia. The tree or trees which yielded amber are not known. Some authorities consider that the bulk of it was produced by a tree belonging to the *Coniferae* and named *Pinites succinifer*; but, in the absence of definite information, this is simply speculation. Much of the European supply is washed up by the waves from deposits which are now under the sea. In West Prussia, however, there are some deposits inland of great extent and these are worked by a regular system of mining, which has a great resemblance to gold mining in its methods. In the district of Samland, containing the towns Wanssen, Grosskuhren, Hubnicken, Palmnicken, Kraxteppelin, Krieslacken, and a few other places, the amber deposits are found in a kind of blue earth, at a depth of about 108 feet from the surface and about 46 feet below the level of the sea; the thickness of the bed is from 8 to 28 feet, of which the lowest portions only are worked. The mining operations are carried on by means of shafts and levels, much as coal mining is done in this country; great precautions, however, have to be taken to prevent inrushes of seasand and water, the ground above being very loose and treacherous. The blue earth is taken to the surface and is there washed in a long slightly inclined trough, the entrance end of which is covered with a grating having apertures about 3 inches in diameter. The large masses are carefully broken up by hand; at intervals of about 6 feet men are stationed with nets to catch all the pieces of amber as they pass down the trough; finally, the waste or tailings pass from the trough through a sieve having apertures of about one-third of an inch in diameter which, while allowing the earth to pass through, retains the amber. At some places jiggging machines with sieves having a mesh of about one-eighth of an inch are used with satisfactory results. About 12,500 tons of earth per month are treated and yields about 156 cwt. of amber at an average cost of about 4s. per lb.

On the coast amber is obtained from deposits under the sea by means of nets, diving and dredging; in the latter case the dredged material is washed as above described.

Amber is found in many other localities, but to a much smaller extent; it is often washed ashore on the coasts of Norfolk, Suffolk, Essex, and Sussex, but the quantity is too precarious to make amber-collecting a profitable industry. It is also found in some sandy deposits in several London localities, but it is scarce. In several localities in France it is found in small quantities.

Among the mountains of Roumania amber is found in workable amounts and of a fair quality. In America there are many deposits, some of which are worked, while there are doubtless many others not discovered. In one particular instance (the amber from Vincent-town, New Jersey) the specific gravity is less than that of water. In North Burmah, in the Hukong valley, amber is found at an elevation of 1,050 feet above the sea and is regularly mined for.

Amber is found in commerce in pieces varying much in size, form, colour, &c. That which is got from mines is usually angular; sea amber is more or less rounded and pebble shaped. It varies in colour very much, from a dull white through pale yellow, to brown, blue, green, and red. In commerce amber is classified according to size, the largest pieces being the most valuable. The palest in colour are best and are mostly used for ornaments, &c., while the darkest, which are of the least value, are chiefly used for varnish making. The following varieties are recognised in the trade:—1. "Shining;" pale yellow or greenish, very bright. 2. "Bastard," opaque, darker in colour. 3. "Bone colour;" dull white; this variety is usually very rich in succinic acid, and, hence, is mostly used for preparing that body. 4. "Agate colour." 5. "Impure;" it contains remains of flies and other insects, vegetable matter, &c. 6. "Cloudy;" this is rather unequally coloured, but is mostly light yellow. 7. "Transparent;" it has various colours. The value of amber depends on the size of the pieces, colour, transparency, &c. For varnish making, as a rule, only the small dark coloured pieces are used, as these are the cheapest.

Amber has a specific gravity of 1.074 to 1.094; it is insoluble in water, ammonia, carbon bisulphide, petroleum spirit, benzene, and acetic acid; slightly soluble in absolute alcohol, turpentine, ether, chloroform, and some essential oils. Boiled in either linseed oil or rape oil for some hours it is softened and can then be moulded, but it is not dissolved. It has a high melting point, about 310° to 320° C. (600° to 615° F.). When distilled it yields succinic acid, amber oil, and a solid residue. The amber oil has a more or less turpentinous composition, a specific gravity of 0.9606 and forms about 23 per cent. of the resin. The melted resin is soluble in hot linseed oil, chloroform, ether, benzene, petroleum spirit, and turpentine, but is insoluble in alcohol. When heated just to the point of fusion for a short time the amber is altered and becomes soluble in turpentine, oils, and other solvents; this property is taken advantage of in varnish making. Amber yields the best varnish of any of the resins;

it gives a firm yet elastic coat and one which resists the action of the atmosphere exceedingly well, but as it is rather dark and expensive it is rarely used.

Animi.—Animi is the varnish resin *par excellence*. No other resin at all approaches it for the brilliance and durability of the varnish it will make, its nearest competitors being the copals. It is used in making the best quality of coach varnishes.

Animi is imported into England from Zanzibar, although some inferior resin sometimes finds its way through Aden, Bombay, and other Indian ports.

Animi is found in two forms—"fossil," which is by far the best, and "recent" or "virgin," which is used locally and in India for making inferior varnishes. Both these forms are derived from trees, the specific tree which yielded the fossil resin is not known, but it is possible that it may be the same as now yields the recent resin.

"Fossil" animi, known to the natives who procure it as "sandarusi," is found in many localities, but especially in the coast districts of the island of Zanzibar and on the neighbouring mainland. It occurs in patches only at a depth varying from $1\frac{1}{2}$ to 3 feet below the surface, generally in a red soil and covered with decayed vegetation. Although found in soils of other colours than red, yet the Arabs who collect it aver that the red soil resin is by far the best and they rarely search for it in other places.

The resin is only searched for during the rainy season, which extends from April to October, the ground then being sufficiently soft to permit of its being probed with a sharp-pointed rod. During the dry season, which occupies the remainder of the year, the ground is too hard to permit of this being done. The method of working is comparatively simple. The resin collector takes the iron rod and probes with it in what he may consider by experience to be a likely spot, and the presence of the resin is readily ascertained; then a hole of about 6 inches in diameter is dug and the resin taken out. The resin thus collected is stored until the end of the rainy season, when it is transported to Zanzibar and there sold to the resin merchants. The amount collected is comparatively small, generally averaging 1 lb. per day for each man engaged, although it would be quite possible to collect more.

The resin as it is found is covered with a red crust formed by the decomposition of the resin and more or less amalgamation with the red soil; this is removed when the resin reaches the resin merchants, usually by a method of scraping and treating with an alkali, when a peculiarity of gum animi makes its appear-

ance—that is, the so-called goose skin. The surface of the resin is found to be more or less covered with a regular pattern of indentations closely resembling the skin of a goose when it has been plucked; whence its name. This appearance is caused by the impression of the cellular structure of the tree in which the resin was originally deposited. The merchants at Zanzibar sort the resin into various qualities before they export it to this country.

“Recent” or “virgin” animi is collected direct from the trees or picked up on the surface of the ground immediately under those trees. The tree which yields this recent resin is the *Trachylobium mossambicense*, although this is a matter of doubt. The Arab name for the tree is “shajar el sandarus,” but different tribes give it different names. This variety of animi has a pale colour, a very smooth surface, and, usually, a long tear shape. The tree is a most prolific producer, every part seeming to be so charged with resin, that the wounding of any part of the tree immediately causes a flow of and a deposit of the resin in that part, a fact of which the Arabs of the districts where it grows are not slow to take advantage. The resin is called by them “chakazi”; it is soft, not unlike gum thus in consistency, of a dull appearance and of small value; it is imported to India for making poor varnishes.

Animi occurs in homogeneous pieces of various sizes, although none are very large; it is quite transparent and of a yellowish or brownish-yellow colour; sometimes it contains the remains of insects. It is so hard that it cannot be scratched with the nail, and breaks with a more or less conchoidal fracture. The specific gravity of animi is about 1.062 to 1.068.

It is nearly insoluble in all ordinary solvents, which at the most cause it to swell a little; ether dissolves part, petroleum ether causes it to swell to a white mass, alcohol has a similar action, chloroform partially dissolves it. With any solvent but a small part dissolves. On this point authorities differ much, probably from the fact that they were not using a genuine sample of animi. Animi is not affected by boiling with caustic soda or acids. The properties here given refer to the fossil variety.

When animi is distilled it gives off, at first, dark brownish vapours, but when the resin is quite melted, which occurs at a temperature of from 240°C. to 250°C. (450° to 465° F.), no appreciable vapours are given off; the rosin loses from 20 to 25 per cent. of its weight, of which about 2 per cent. comes off as water and 18.5 per cent. as a brownish coloured oil, having a strong empyreumatic odour; the oil has a specific gravity of 0.9081, and is

soluble in benzene, ether, petroleum spirit, and turpentine, but is insoluble in alcohol. It has slightly acid properties and contains a small quantity of bodies capable of combining with caustic soda, but the main bulk has, probably, a terpene composition. The residue in the retort sets, on cooling, to a hard, clear, transparent resin, soluble in benzene, chloroform, petroleum spirit, and turpentine to clear solutions; in ether it gives a cloudy solution; it is insoluble in alcohol, but soluble in hot linseed oil.

Copal.—The term “copal” is now used very frequently as a generic term, covering a number of resins of various origin. Strictly speaking, it should, when used as a class name, only include resins, of which animi may be taken as a type; but it is made to include resins such as Manila copal, which has very different properties. Accordingly, copals are often divided into two groups—“true copals” and “false copals.” The former includes animi and the copals found on the West Coast of Africa, and perhaps also kauri and the Demerara copal. The latter group includes Manila copal, dammar, and a few others. “True copals” are hard, lustrous resins, insoluble in solvents, and require to be fused before they can be made into varnish. The “false copals” vary very much in their properties—some are hard, as dammar, others are soft, as Manila copal. They are more or less soluble in solvents like alcohol, benzol, turpentine, &c.

Gum copal is a product of vegetable origin found on the West Coast of Africa, over a district extending from latitude 8° N. to latitude 4° S., a distance of some 700 miles. In this district very large quantities of copal is found, as a fossil resin, in the ground at various depths up to about 10 feet. It is dug for by the natives during the rainy season only, which extends from March to May. Generally it is found in the superficial strata of marl, clay, and sand, which are sufficiently soft in the wet season to permit of being easily worked, but in the dry season they are too hard for the negroes to dig into with the rather primitive tools they use. The botanical origin of copal is not known with certainty. Some authorities assign it to a tree called *Guibourtia copallifera*, while it is quite possible that it comes from a variety of species; certainly, no tree which is at present growing on the copal coast yields this gum. This fact, together with its occurrence in very recent deposits and the existence of the pebble copals in the beds of the rivers of this district, show that it is most likely to be the produce of various species of trees which have grown or now grow in inland districts. Probably, as the interior of the copal districts become better known, the source of the resin will be discovered. After

the resin has been collected, it is carried by the natives, along with other produce which they collect at the same time, to the ports for export to Europe, America, &c. The principal ports from which copal is thus exported are Sierra Leone (from which the best copal is obtained), Accra, Benin, Gaboon, Loango, the Congo, Angola, Benguela. The copals obtained from these places are not identical in properties, some being harder than others.

Sierra Leone copal is the best quality of copal imported from Africa. It usually comes over in the form of rough angular pieces, almost colourless or, at the most, having a faint yellow colour. It is hard, has a specific gravity of 1.054, is quite insoluble in all the ordinary solvents, and only becomes soluble after it has been fused, the melting point being 400° F. It is very lustrous, and makes a first-class and very durable varnish. By careful selection of the resin used, pale varnishes can be made from this copal. It is the product of the copal tree *Copalifera Guibourtiana* (*Guibourtia copallifera*), from which much of it is collected at the end of March, before the rainy season sets in.

Pebble copal also comes from Sierra Leone. It occurs in the form of rounded pieces, varying slightly in size, and is mostly colourless; but some samples are slightly coloured, mostly pale brownish-yellow. It is very hard (perhaps the hardest of the copals), and its specific gravity is about 1.055. From its form it has evidently been transported from the interior by the rivers, in whose beds it is now found. Owing to the supply being small and somewhat uncertain, varnish makers are rather shy of using Pebble copal, although it makes a good varnish resin.

Angola copal is found in the three districts of Angola, Benguela, and Congo, the copal from which are so much alike that in commerce they are classed together as "Angola copal," or, as it is often called from its colour, "red Angola copal." It is generally in the form of globular pieces, although flat pieces are often met with. The size is usually about 1½ to 2 inches, but large pieces about 5 to 6 inches have been found. This copal is generally covered with a reddish crust about one-sixteenth of an inch thick. When this crust is removed, the resin is usually found free from colour or, at most, has a faint yellowish colour; occasionally brownish pieces are found. The darker coloured pieces are often the freest from air bubbles—bits of bark, wood, &c., which are often found in the colourless variety. These, therefore, command a higher price in the market. Angola copal is not so hard as those above described. It yields a good quality of varnish, brilliant and durable. Its specific gravity is 1.065.

Angola copal only comes into commerce in small quantities; almost too small to induce varnish makers to use it.

Gaboon copal is found in rounded, flattened pieces, varying in size from about $\frac{1}{2}$ to $2\frac{1}{2}$ inches; in colour it is the darkest of the copals—a sherry colour; transparent; but, as a rule, not homogeneous. The surface is generally smooth, but some pieces have a crust, which is sometimes striated.

Loango copal differs from other copals in being found in the form of cylindrical pieces, which are evidently only portions broken off much larger pieces; two varieties are known, red and white; the former is, as its name indicates, of a reddish or faint brownish colour, and is rather larger than the latter and more cylindrical in form; the white varies in colour from colourless to faint yellow. The red is the best and, on account of its being more homogeneous, more lustrous and harder than the white, is both more in demand and brings a higher price in the market.*

Demerara Copal.—This fossil resin comes from the locust tree, *Hymenaea Courbarii*, of British Guiana. It is collected much in the same manner as animi and copal, and, when freed from the outer crust, has a splendid lustrous appearance, being quite clear and transparent, perfectly homogeneous and often occurring in large masses; pieces of from 10 to 12 lbs. weight are frequently found, while a mass weighing at least 60 lbs. was shown at the Manchester Exhibition in 1887.

It has a specific gravity of 1.030 and melts at about 240° to 250° C. (450° to 465° F.); it gives off a large proportion of volatile oil and gas, and leaves but little solid resinous matter as compared with animi; thus, weight for weight, it does not make as strong a varnish as animi or copal, but, allowance being made for this fact, it is an excellent varnish resin. It is also known as Demerara animi.

Ether dissolves it, alcohol causes it to swell to a white jelly, chloroform causes it to swell and dissolves a part of it, petroleum ether causes it to swell to a white jelly.

✓ **Kauri.**—This is a very important copal-like resin found in New Zealand in large quantities, which has only comparatively recently come into use as a varnish resin. It is also known as Cowdee gum, Kowree, Cawree gum; there are various other ways of spelling the name.

This resin is the product of various species of New Zealand pine trees, chiefly from *Dammara Australis*, which yields by far

* Copal is slightly soluble in turpentine on long digestion with the solvent, but it is nearly insoluble in other media, which at the most only cause it to swell, while but a small portion passes into solution.

the larger proportion of the resin which finds its way into the market. Other species are *Dammara ovata* and *D. Cookii* of New Zealand, while in Queensland, *D. Brownii*, and in New Caledonia, *D. lanceolata*, yield the resin in small quantities. Most of the resin which finds its way into use is dug out of the ground. It is found all over the Colony. At present there is no regular organised system of searching for the resin, but a very large, although variable, number of persons, mostly natives, are engaged in the collection of it. The resin is found at various depths, from a few inches to several feet below the surface, on which, however, there are no indications of its presence below; large pieces are often turned up in ploughing cultivated lands. The resin digger uses two tools, a spear, which is a long, sharp-pointed, wooden-handled steel rod of about $\frac{1}{2}$ inch in diameter, and a spade. With the spear he pierces the ground and feels for the resin; experience soon tells him when he has touched a piece, and then he digs down to it; the find may only be a small one, or, as occasionally happens, very large pieces are found. The surface of the resin is covered with a thick crust of decayed vegetable and resinous matter which is removed by the digger before he sells it to the merchant. Besides the fossil resin, kauri is also obtained from the living trees; such resin is known as "young" kauri, and it differs from fossil kauri in being almost colourless and softer. The trees, when they are cut, bleed profusely and yield a pale yellowish viscid fluid which dries into a hard resinous mass; both old and young trees yield the resin, and it is no uncommon thing to find in old trees deposits of the resin. The stumps of felled trees soon become covered with a thick layer of kauri resin. The trees are fast disappearing, and soon no "young" resin will be obtainable.

Kauri comes into the market in pieces varying much in size, from a few inches to two feet, and in weight, from 1 lb. to $\frac{1}{2}$ cwt. The best quality is known as "dial" kauri, but many varieties are recognised in the trade. In colour it varies but little, being mostly of a pale amber or pale brown. Some samples are homogeneous, others are more or less streaked; the former kind are usually clear and transparent, while the latter are often opaque. In lustre it varies from glassy to opaline. It breaks with a conchoidal fracture, and freshly-broken pieces have a fragrant odour which is very characteristic. The taste is pleasant and aromatic. It is used by the Maoris of New Zealand as a chewing gum, especially the "young" kauri. The specific gravity is 1.050, New Caledonia kauri being rather heavier than New Zealand kauri. It melts easily at from 360° F. to 450° F.; and

on distillation it gives about 1·4 per cent. of water and from 16 to 20 per cent. of oil of specific gravity 0·9224, soluble in ether, but insoluble in alcohol, and caustic soda.

Kauri is used in varnish making as a rival to copal, but, although the varnish it yields is a good one, yet it is far from equalling copal varnish, not being so durable. When exposed to the weather it has a tendency to become powdery, but, being hard, it is largely used in varnishes for interior work and, to a limited extent, in the preparation of ornaments. Petroleum spirit, alcohol, turpentine, and benzol cause kauri to swell up to a white opaque mass dissolving a portion of it; chloroform only partially dissolves it, but ether completely. After melting, the gum is soluble in ether, petroleum spirit, turpentine, benzol, and chloroform to clear solutions. There are, however, variations between different samples of kauri in their solubility in these media.

Sandarac.—This resin has quite different properties to the copals above described. It is used in making both oil and spirit varnishes, although for the former kind its use is decreasing. It is also known as gum juniper. It is the produce of the *Alerce* tree, *Callitris quadrivalvis*, a tree indigenous to North Africa, in the mountain regions ranging from the Atlantic coast to at least as far East as Eastern Algeria, but possibly further. The resin is found exuding naturally from the trees. The Moors who collect it are in the habit of making small incisions in the bark of the tree for the purpose of increasing the amount of flow of the sap, and, therefore, the quantity of resin; after collection it is taken to Mogador for export to Europe.

Sandarac occurs in the form of short cylindrical pieces or tears, which are sometimes agglomerated together; in colour it is a yellowish white; it is a comparatively hard resin, being about equal to kauri or rosin in this respect; it melts easily at about 300° F. (150° C.), and breaks with a clean, lustrous fracture. The specific gravity is 1·038 to 1·044.

It is soluble in alcohol and ether, partially soluble in benzol, petroleum spirit, and turpentine, but very slightly soluble in oil before fusing, yet readily so after fusing. It is used in making pale spirit varnishes, and is valued on account of the hardness and lustre of the coat it forms.

Rosin or Colophony.—The name of this body is spelled rosin or resin; the former is more in accordance with the pronunciation of it and will be adopted here; the latter is liable to confusion with the generic name for the group of resins. Colophony is rarely used. Rosin is obtained in the distillation of turpentine

from gum thus (see p. 361) and is left behind in the still after the turpentine has come over; the melted rosin is run from the stills into moulds or barrels to cool. Rosin comes into the market in the form of large pieces, generally homogeneous, varying in colour and transparency; the best quality is known as "window glass" rosin, and is a pale amber in colour, perfectly clear and transparent; "common" rosin is much darker in colour but is still homogeneous, clear and transparent; "black" rosin is very dark, almost approaching a black, and opaque. These varieties are dependent upon the quality of the original resin from which the rosin has been made; the so-called "virgin" resin gives the best rosin, while the resin collected later on in the season gives common rosin, and the scrapings of the resin from the bark, &c., give black rosin. Rosin is slightly heavier than water, its specific gravity being 1.044 to 1.100; it easily melts; at about 177° F. it softens, and at 212° F. it is quite fluid; "window-glass" rosin forms a clear, limpid, yellow liquid. It is insoluble in water; is soluble in about eight times its weight of alcohol; in benzol, coal-tar naphtha and acetone in almost any proportion; soluble in turpentine, ether, and most oils. It is also soluble in boiling solutions of the alkaline carbonates or hydroxides, becoming hydrolised and taking up the elements of water to form abietic acid, with which the alkalis combine to form the rosin soaps so largely employed in the soap industry. Rosin is a mixture of two acids bodies, pinic and sylvic acids, which are isomeric and have the formula $C_{20}H_{30}O_2$. Some authorities consider that the composition of rosin is not that of a true acid, but an anhydride, abietic anhydride, which will take up water to form abietic acid.

When distilled rosin yields a small quantity of acid water, spirit (see p. 372), a heavy oil (see p. 357), and a residue of pitch. It is used in making common oil varnishes, in making some cheap spirit varnishes, and in naphtha varnishes. By itself it leaves rather a hard, brittle, and lustrous coat, but tempered with some oil or soft resin it makes a durable varnish, not, of course, approaching the copals or kauri in this quality.

A solution in hot alcohol deposits crystals of sylvic acid on cooling. Nitric acid converts rosin into terebic acid, $H C_7 H_9 O_4$, which is soluble in water.

Asphaltum.—Asphaltum or native bitumen is used in the varnish manufacture in the production of black varnishes, blacks, japans, &c. It was originally obtained from the shores of the Dead Sea, and this variety is specially designated Bitumen of Judea and Egyptian asphaltum, but it is imported from other

places, Altona in Albania, Coxitambo in South America, and Barbados, while there is an almost inexhaustible supply in the great lake of Trinidad. Asphaltum, when pure, is a blackish-brown solid, breaking with a conchoidal fracture, the surfaces being bright and lustrous. At 100° C. (212° F.) it melts to a black liquid having a strong pitchy odour. It burns with a bright somewhat smoky flame. In water and alcohol it is insoluble. It dissolves readily in coal-tar naphtha, but not so readily in turpentine. Its specific gravity varies from 1.00 to 1.20.

When used alone, simply dissolved in naphtha or turpentine, it dries with a gloss, with, however, a very brittle coat that in time begins to crack very much; on this account asphaltum, formerly much used by artists, has of late years been abandoned for oil painting.

In making japans and black varnishes its brittleness has to be overcome by the use of oil and other gums. Asphaltum is generally considered to be a product of the decomposition of animal and vegetable organic matter.

Artificial Asphaltums are now made by mixing together in various proportions coal-tar pitch, wool pitch, rosin pitch, and other pitches obtained in the distillation of animal and vegetable oily products. These are very useful in making cheap black varnishes, but considerable care must be taken in their selection, as many of the pitches, especially those from petroleum and paraffin, will not dry.

ETHEREAL-VARNISH RESINS.—This is an important group of resins, which are more or less soluble in such solvents as benzol, coal-tar naphtha, turpentine, ether, acetone, &c., and which are used with these solvents to make varnishes for special purposes. This group includes:—

All oil varnish resins after they have been fused.	
Dammars.	Rosin.
Mastic.	Manila copal.
Sandarac.	

Some of these have already been described.

✓ **Dammar.**—Under the name of Dammar there is imported into this country, for making varnishes, several kinds of resins, principally from Siam, and which do not differ very much from one another in their properties.

1. *Singapore dammar*, also known as white dammar, is the true dammar. It is the produce of the Amboyna pine, *Dammara orientalis*, a large tree indigenous to Malacca, Java, Sumatra, Borneo, and the Malaccas, growing in the hill districts; in Java

it is cultivated to a small extent. The supply principally comes from Java through Singapore. The resin exudes from certain excrescences which grow a short distance above the root of the tree; in Sumatra and other places the resin exudes out in large quantities, while in other localities the natives make incisions in the excrescences to promote the flow of the resin; large quantities of the resin are also found in the river courses, having probably fallen from trees growing on the sides of the rivers. The resin exudes also from the upper portions of the trees, branches, &c.; the resin from the roots is usually in the form of large rounded knotty pieces, while that from the branches is more or less stalactitic in form.

Singapore dammar comes into commerce in the form of nodules, varying in size from $\frac{1}{2}$ an inch to $1\frac{1}{2}$ inches, sometimes larger, covered with a powdery crust; the interior is usually clear and transparent and is nearly white in colour, at the most it has a faint straw tint. It is friable and breaks easily with a powdery fracture. It is not quite so hard as copal, but is harder than rosin; when fresh it has a faint agreeable balsamic odour, which disappears on keeping. Its specific gravity is 1.062 to 1.123. It is soluble in turpentine, ether, petroleum spirit, chloroform, and in oil. That from Batavia dissolves more freely than the Singapore variety. The melting point of both is about the same, 260° to 300° F. It is used in making varnishes for coach and cabinet makers, for paper, for pictures, and it is used dissolved in benzol for mounting microscopic objects. Dammar gives a pale, hard varnish with a fair amount of lustre. It has the defect of being rather friable, so that if, when dry, the coat is rubbed with the fingers it becomes powdery.

2. *Rock Dammar*.—This resin, which is almost indistinguishable from the last variety, is the produce of two species of *Hopea*—viz., *Hopea odorata*, which grows in Burmah, about Rangoon, Pegu, Martaban, and Tenasserim; and *Hopea micrantha*, a native of the Malay States of Malacca, Sumatra, Borneo, and Labuan. There are great differences between the resins yielded by these two trees; that from *odorata* generally occurs in rounded pieces about the size of walnuts, and is pale in colour; colourless pieces are often found. The *micrantha* resin is rather darker and a little harder. Rock dammar is soluble in turpentine, and other solvents, and is of equal value with the Singapore and Batavian dammars.

3. *Sal Dammar*.—This is the produce of the Sal tree, *Shorea robusta*, which grows on the southern flanks of the Himalaya mountains along nearly their whole extent; it is also found among the hills of West Bengal, in Borneo, Sumatra, and in the

Malaccas; so that its range is a wide one. It occurs in long pieces of a stalactitic character, rather brittle, mostly of a pale cream colour, more or less opaque and striated as if the pieces were formed by the separate flow of different streams of liquid resin, each of which solidified before the succeeding one had begun to run. Its specific gravity ranges from about 1.097 to 1.123. It is soluble in ether, benzol, and turpentine, partially soluble in alcohol; the solutions are not quite clear, but always have a more or less turbid appearance.

It is not often met with in the English market. It is used in making paper varnishes and tracing paper, as, when dissolved in turpentine, it gives a good, pale, hard varnish which dries well and is elastic.

4. *Black Dammar*.—Black dammar, known in India as kala dammar, is the produce of several species of *Canarium* trees, principally *Canarium strictum* which grows in the Tinevelly district. The resin is collected in a very different manner from that adopted with other resins; the natives in the hot season make a number of vertical cuts just above the base of the trunk and then set fire to the tree below these cuts; by this means they kill the tree, which is now left for two years, at the end of which time a quantity of resin will have exuded from the trunk; this resin is collected in the months of February and March. The resin flows for some years after the tree has been killed. In the Coimbatore district a somewhat different system is used to collect the resin; firewood is piled round the tree to the height of about 1 yard; this is fired and allowed to burn out; the resin subsequently exudes from the tree to about as high as the flames of the fire extended. The flow lasts for 10 to 12 years, and principally occurs during the months of November and April; generally, the resin is collected in January.

A tree will yield 200 lbs. of resin. Black dammar occurs in large black or brownish-black pieces, which are opaque when viewed in the mass, but in thin slices are transparent; it is homogeneous and vitreous in structure, breaking with a clear, conchoidal fracture. Specific gravity, 1.090. It is not very soluble in cold alcohol, but dissolves in hot alcohol; it is soluble in turpentine. On distillation it yields a large quantity of oil resembling rosin oil.

It is used in India for making varnishes, but in this country it is rarely seen, and it is doubtful whether there would be much demand for it, as, on account of its colour, it cannot be used for many kinds of varnishes and for some purposes it cannot compete with the cheaper rosin.

Mastic.—This resin is the product of the lentisc tree, *Pistachia lentiscus*, which grows in all countries washed by the Mediterranean; Spain, Portugal, Italy, Greece, the islands on the Greek, Turkish, and Levant coasts, North Africa, &c. The principal portion of the mastic comes from the district around Chios, one of the principal islands of the Greek archipelago. The mastic tree is shrubby, growing to a height of from 4 to 5 feet; the bark contains numerous resin vessels from which the resin is exuded in fairly large quantities on making excisions. About the months June to August the natives of the mastic district make many vertical incisions in the bark of the stem and branches, keeping these open during the period mentioned; the resin flows freely and soon becomes dry and hard; about two or three weeks after the cutting the resin is collected in small paper baskets, great care being taken to keep the resin clean; with the same object the ground below the tree is kept free from loose dirt, so that any resin which may accidentally fall from the tree may not get dirty. The lower branches of the tree frequently exude resin spontaneously; this is considered to be of a superior quality and is kept apart from the rest. A tree in good condition will yield from 8 to 10 lbs. per annum, but in the rainy season only $\frac{1}{4}$ lb., showing a considerable difference in the yield, which is much less in such seasons.

Mastic is sent into commerce in several forms:—1st, Cake, which is in the form of large pieces, and is the best quality of mastic; this variety is largely used as a chewing gum in Turkey. 2nd, Large mastic; this variety is mostly used as a chewing gum. 3rd, Small mastic; this occurs in small tears, and is the variety mostly met with in this country and which is used for making varnishes and for other industrial uses.

Mastic comes in the form of small tears of from $\frac{1}{4}$ to $\frac{1}{2}$ an inch long, mostly of a pale yellow colour, but sometimes they have a faint greenish tint; old specimens are darker than fresh samples. The outer surface of the tears is often powdery and the tears appear to be opaque; sometimes the tears are quite clear and transparent. Mastic is rather brittle and breaks with a conchoidal glassy fracture. Fresh mastic has a pleasant balsamic odour. It softens readily when placed in the mouth, a character distinguishing it from sandarac, which resembles it in form. Its specific gravity is about 1.056 to 1.060; it melts at from 105° to 120° C. (221° to 248° F.); but softens below the temperature of boiling water. It is soluble in turpentine, alcohol, chloroform, and acetone, but not in petroleum spirit. It is used in making varnishes for pictures; a combination of mastic varnish and

linseed oil forms the peculiar artists' medium known as megilp.

Manila Copal.—This resin is the product of various species of trees growing in the Philippine Islands. It is gathered by the inhabitants and exported, chiefly from Manila, the principal town of the islands; hence it is called Manila copal. The use of the term copal is misleading, as it does not resemble the copals in its properties. The only similarity is that, like these, it is of vegetable origin.

Manila copal occurs in small pebble-like pieces of a pale brownish-yellow colour, varying slightly in different samples. Its specific gravity is about 1.062. It differs very much from the true copals in all its properties; it is much softer; melts at from 230° to 250° F.; and at a temperature a little above this begins to distil over, the distillate consisting of both acid water and an oil having a very empyreumatic odour.

Manila copal swells when placed in petroleum spirit, and a little dissolves; it is soluble in ether, and partially soluble in benzene, chloroform, and turpentine; in alcohol it dissolves to a turbid solution. Manila copal which has been melted is much more soluble than fresh copal, the fused gum being freely soluble in all solvents except alcohol, which does not dissolve it any more freely than the fresh resin. It is used in making spirit varnishes, more for the purpose of giving elasticity to other resins than for any brilliancy and hardness it possesses of itself. It leaves a faint durable coat behind it, and is much used in the preparation of enamel paints.

SPIRIT-VARNISH RESINS.—This group of resins comprises those which are soluble in alcohol or methylated spirit and they form an important and valuable group. The spirit-varnish resins include:—

Lac.	Mastic.
Manila copal.	Rosin.
Sandarac.	Melted resins.

Some of these have already been described, leaving but a few that require to be dealt with.

✓ **Lac** is a most important product from many points of view. In its origin it differs from the resins previously described. Lac is a resinous incrustation found on the twigs of many species of Indian trees, the number and variety of which has not as yet been properly ascertained. The following is a list of the most important lac trees:—Palas or dhak tree, *Butea frondosa*; the peepul tree, *Ficus religiosa*; the koosum tree, *Schleichera trijuga*;

Acacia arabica, *Acacia catechu*, various species of *Croton* (*lacciferum*, *draco*, *sanguiferum*), *Butea superba*, various species of *Ficus* (*elastica*, *cordifolia*, *venosa*, *villosa*, *indica*, *glomerata*, &c.), *Mimosa cinerea*, &c. All the lac trees have a very gummy or resinous sap. The lac is not a direct product of the tree, but is formed from the sap by the female of the lac insect, *Coccus lacca*. The insect punctures the bark of the tree and commences to secrete the lac, forming it into cells in which it lays its eggs; the insect becomes in time completely imbedded in the lac, breathing by means of fine filaments which it sends to the surface for that purpose; when it has laid its eggs it dies; after the young insects are hatched they puncture the lac and swarm over the twig or tree branch; the males impregnate the females, which latter then proceed to secrete lac as their ancestors did before them; the insects do not move from the portion of the tree on which they first swarmed. The tree supplies nourishment to large quantities of lac insects, but at the expense of its own vitality; for, after a time, it begins to decay and then it ceases to be able to support any more insects. The distribution of the insects from place to place is probably, in the absence of any effort by the insects themselves, effected by the agency of other insects and of birds who carry the young from tree to tree; of late years artificial propagation has come into existence.

The principal portion of the lac of commerce is grown in India, but it is also obtained from other Asiatic countries. The lac of Siam has a great reputation for quality. It is also found in Ceylon, Burmah, China, Malay archipelago, and other localities. In India lac grows principally in the province of Bengal, the capital of which is a great emporium for lac in all its states; in this province the jungle districts of Chota Nagpore, Orissa, and Beerbhoom, are the chief localities. It is collected twice a year, from about the middle of October to January, and from the middle of May to the middle of July. In the Scinde State it is found abundantly in the forests surrounding Hyderabad, where it chiefly grows on the babool tree, *Acacia Arabica*; the tree, however, is not attacked by the insects while it is in the full vigour of its growth, but as soon as it begins to wither the insects attack it and thrive well upon it, eventually killing it. The period of gathering the lac extends from October to the following April. It is mostly consumed locally, being used to produce the famous lacquered ware for which Hyderabad is noted. Assam is a great lac country, and lac is collected in large quantities; much is used locally, but still a large quantity finds its way to Calcutta for export. In the Central Provinces large quantities of lac are pro-

duced, in the east districts especially. Jubbulpore is a great centre for lac; the district itself supplies a great deal, and much comes into the city from Rajpore, Bilaspore, Mundla, and Sangor; most of it is used locally in the manufacture of ornaments of various kinds, and the rest is sent to Bombay for export. Sumbulpore and Mirzapore are also places of note in the lac trade. Sobhapore, in the Hoshungabad district of the Central Provinces, is a large centre of the lac trade, the lac coming into it from Futtehpoore, Bankheri, the Nerbuddha Hills, Nursinghpore, and other places. The towns of Hoshungabad and Babai are also places of trade in lac. From Oudh comes supplies of lac which is found principally in the forests of the south-eastern districts, where it grows chiefly on the *Ficus religiosa*. In the Punjab lac is found in large quantities, although of inferior quality; it is sent to Calcutta for export. There are many other localities where lac is obtained in large or small quantities; some of it is used locally for a great variety of purposes, and the rest is sent to one of the principal seaports for export to Europe.

Lac comes into commerce as—

- | | |
|---------------|----------------|
| 1. Stick lac. | 4. Button lac. |
| 2. Seed lac. | 5. Garnet lac. |
| 3. Shellac. | |

Another lac product is lac dye, which at one time was largely imported into Europe for dyeing purposes, but since the introduction of the coal-tar colours it has completely fallen into disuse.

1. *Stick lac* is the crude product just as it is taken from the trees; it rarely comes into English commerce, as it does not pay to export useless twigs of trees. Stick lac is in the form of short pieces (about 2 to 3 inches long) of the twigs with the lac incrusting them; it is cut into these lengths for convenience of carrying, &c. Stick lac is sent from the forests and jungles, where it is collected, to the different towns for manufacture into lac products. The process of manufacture is very simple, and is carried out in a very crude manner, although of recent years improvements have been made with the view of increasing both the quantity and quality of the products.

The process of lac manufacture consists in first separating the lac from the woody portion of the stick lac; this is done by placing the stick lac on a table and passing a roller over it; the lac being brittle is broken and separated from the wood almost entirely; the little that is left adhering to the wood is picked off by hand. The wood is thrown away, the lac is taken, broken into small pieces about $\frac{1}{4}$ inch in size, placed in large tubs with

warm water, and worked by the workmen getting into the tubs and treading; this process extracts the colouring matter from the lac, and is continued until the wash waters remain clear. The lac left behind is known as "seed lac." The liquor is boiled down dry, and the resulting solid mass is formed into cakes and sold as "lac dye."

2. *Seed lac*.—This is the partly manufactured product obtained, as described above, by treating stick lac with water; this is sometimes sold for various purposes, but it is mostly manufactured into the other lac products.

3. *Shellac*.—This is the principal lac product and the variety which is mostly used in this country for varnish making. Shellac is made from seed lac as follows:—The seed lac is dried and placed in large bags made of cotton cloth of a medium texture. Two men take hold of the bag of seed lac, one at each end, and hold it in front of a charcoal fire; the heat of the fire soon melts the lac, which flows out of the bag, the men assisting the flow by twisting the bag from each end in opposite directions, so as to squeeze the liquid lac out of the bag; the molten lac drops into a trough placed in front of the fire. A cylinder (made of different materials at different localities) of wood, with the upper half covered with brass, or it may be made of porcelain or of the finely polished stem of the plantain. This cylinder is set in a somewhat inclined position, and the operator, taking up a ladleful of the molten shellac from the trough, pours it on the upper surface of the cylinder, while an assistant, by means of a leaf of plantain, spreads the melted material over the surface of the cylinder. It soon sets, when, by means of a knife, it is stripped from the cylinder, and is then ready for sale as "shellac."

The best quality of shellac has a pale and bright orange colour, and is hence known as "orange shellac;" but in the market many qualities are recognised distinguishable from one another by their colour, by their freedom from dirt and grit, and by their transparency.

4. *Button lac* is only different from shellac in form. Instead of being made into thin sheets the melted shellac is poured on to plates in such a manner that it sets in the form of large round flat pieces, which, owing to their thickness, appear of a dark brown colour; but are of a dark ruby colour on being looked through.

5. *Garnet lac* is very similar to button lac, but is made into thick flat pieces, which, in colour, resemble those of button lac. Usually the quality of lac made into button or garnet lac is not so good as that from which orange shellac is made.

For making varnishes either shell, button, or garnet lac may be used, but the latter two are only used for making the commoner kinds of shellac varnish, where colour is not so much an object; for the best qualities of spirit varnishes only orange shellac is used.

Of late years some improvements have been adopted in one or two large lac factories in India. The lac is better washed, whereby more colouring matter is extracted from the crude lac; then, the appliances for melting and straining and converting the lac into its shell form are considerable improvements on the primitive methods described above.

Lac comes into commerce in three forms—shellac, in thin flakes of an orange colour, varying a little in shade and transparency; button lac, in large round flat masses of a dark colour; and as garnet lac, in irregularly shaped flat pieces of a dark ruby colour. It is rather brittle and easily broken up into small pieces. Occasionally it is artificially coloured with orpiment or mixed with rosin, but such adulterations are rare.

Lac is incompletely or only partially soluble in alcohol or methylated spirit, forming a turbid brownish-orange solution, which is largely sold as French polish and varnish for cabinet and other work.

Lac is only partially soluble in ether, chloroform, and turpentine, while it is insoluble in petroleum spirit. It is soluble in solutions of caustic potash, and of caustic soda to dark red solutions. In borax solution and in weak ammonia it is also soluble, and such solutions are sometimes used as water varnishes. One point of interest in the solubility of shellac in such alkaline liquors is that the colouring matter is first dissolved away from the resin proper, leaving the latter of a pale colour; this property is taken advantage of in preparing white shellac. Chlorine passed through alkaline solutions of lac throws down the resin free from colour. Lac has a specific gravity of 1.113 to 1.214, the darker varieties being the heavier.

Crude stick lac freed from woody matter contains 66.67 per cent. of resin, 6 per cent. of wax, 6 per cent. of gluten, and 10.8 per cent. of colouring matter. In shellac five distinct resins have been separated—(1) resin soluble in alcohol and ether; (2) resin soluble in alcohol, but insoluble in ether; (3) resin slightly soluble in alcohol; (4) a crystallisable resin; and (5) an uncrystallisable resin. These constitute about 90 per cent. of the shellac. There are in addition (6) fatty matter; (7) wax; (8) gum; and (9) colouring matter.

Bleached or White Shellac.—Shellac may be bleached in two

or three ways. One method is to boil ordinary shellac in a weak solution of carbonate of potash, and when dissolved passing a current of chlorine through it; the lac precipitated is collected, melted under water, and then, while soft, pulled so as to give it a fibrous satiny appearance. Another method is to boil the shellac in a weak solution of potash, and, while melted, pulling and working together until the desired whiteness has been attained. Then the shellac is remelted and repulled in clean warm water. White shellac is sold in the form of long cylindrical pieces having a fibrous satiny appearance. It is used for making white varnishes and for other purposes where a white shellac is required; as it is sold in rather a wet condition it is necessary to dry it before using it. It is sometimes considered that white shellac deteriorates on keeping, but this is somewhat doubtful, and there is no apparent reason why it should.

Elemi.—Under this name several varieties of a resinous matter come into commerce which are used as a softener or toughener for varnishes.

1. *Manila Elemi.*—This comes from the Philippine Islands and is the product of a tree known as *Canarium commune* to botanists, which principally grows in the island of Luzon; the supply is sent through Manila. This variety of elemi is white when quite pure and of good quality, although some samples have a grey appearance and others appear to be composed of two or three sorts of resins. The resin is soft and has a granular appearance; when exposed to the air for some time it becomes hard, owing to the evaporation of the volatile oil present in freshly-gathered elemi. The odour is slightly turpentiney. When distilled this elemi yields about 10 per cent. of an oil resembling turpentine in its composition. Elemi begins to soften at about 75° to 80° C., and is quite liquid at 120° C. It is soluble in alcohol and in most other solvents. It is used in varnishes to give elasticity or toughness.

2. *Mexican Elemi.*—This variety is obtained from a tree known as *Amyris elemifera*. In its essential properties it resembles Manila elemi, but is rather darker coloured and harder in appearance and consistency. It is not very common.

3. *Brazilian elemi* is supposed to come from trees belonging to the genus *Icica*, but is not an article of regular importation into this country.

4. *Mauritius elemi* is supposed to come from the tree *Colophonia Mauritiana*, and is stated to resemble Manila elemi in appearance and properties.

Benzoin.—Gum benzoin or gum benjamin is a balsamic resin

which exudes from *Styrax benzoin*, a native of Sumatra, Java, Borneo, Siam, Laos, and other places in the same region. The commercial product comes principally from Siam and Sumatra. The Malays know it by the name "kaminian." In the coast regions of North and East Sumatra it is cultivated from seed. In about seven years it obtains a diameter of 6 to 8 inches and is then ready to be cut. The natives make incisions in the tree and the resin exudes from them very freely, each tree yielding about 3 lbs. annually; for the first three years the product is of first-class quality, of a yellowish-white colour and soft with a fragrant odour; after the third year the product is darker in colour, harder and not so fragrant; after about nine years it is not worth collecting. In the interior regions the resin is collected from wild trees.

The benzoin which comes into England is imported almost entirely from Siam and Sumatra. There are some small differences in the appearance and properties of these two varieties of benzoin.

Siam benzoin comes into commerce in the form of agglutinated, flattened, somewhat opaque, milk white tears or in large agglomerations consisting of white masses distributed through an amber-coloured, rather translucent matrix. It is brittle, and has a strong vanilla-like odour, which is very characteristic. It is readily softened by heat; it is quite soft at 75° C. and fluid at 100° C.

Sumatra benzoin is rather greyer, and is in the form of an agglomerate mass with white tears distributed through a darker translucent matrix. Its odour is not so strong as that of Siam benzoin and it does not melt so easily; it contains more benzoic acid, which comes off in vapour when the resin is heated. In all other properties the two resins are identical.

Benzoin has a peculiar fragrant odour, and is slightly heavier than water; its specific gravity being about 1.092 to 1.145, although some authorities give rather higher figures than these. It melts at a gentle heat and gives off white vapours of benzoic acid with a small quantity of volatile oil. Alcohol dissolves most of it; ether has a slightly less solvent action; while turpentine and petroleum spirit dissolve very little of it. Treated with sulphuric acid, benzoin or an alcoholic solution turn bright red, while with ferric chloride a green colour is produced.

Benzoin finds a small use in varnishes, chiefly on account of the odour which it imparts to the varnish; it is also used in making perfumes, incense, &c.

3rd. GUMS.—The true gums, such as gum arabic (the type of a true gum), gum tragacanth, and a few others are, like the resins,

exudations from trees, and are collected much in the same manner. They differ from resins in one or two important particulars. In the first place, they are more or less soluble in water; some, like arabic or acacia gums, are completely soluble; others, like gum ghatti, are partially soluble; while others again, like tragacanth, are not properly dissolved by water, although acted upon by that vehicle. The true resins are quite insoluble in water. On the other hand, the gums are quite insoluble in alcohol and other similar solvents.

The gums, which belong to the third group of varnish materials, are almost exclusively used for making water varnishes, or (as in water-colour painting and in some kinds of distemper work) as fixing agents to fasten the pigment on to the work.

Besides the gums proper there are used in making water varnishes gelatine or glue, dextrine or British gum and albumen.

Gum Arabic.—The name of this gum is a misnomer, because it would indicate that it comes from Arabia, whereas but little, if any, now comes from that country; probably in early times it may have been obtained from that country, or, at least, imported through it and hence the term "arabic" arose. It is also known as gum acacia, from the trees which yield it; but gum arabic, despite its error, is the name by which it is best known in the trade, and therefore it will be retained here.

The species of *Acacia* are profusely distributed throughout the tropical parts of Africa, Asia, and Australia, and are all gum-producers. The gums vary a little in appearance and properties, but all are more or less soluble in water, and give with that solvent a strongly adhesive mucilage useful for a great variety of purposes. These gums are distinguished in the trade by terms descriptive either of their place of origin or of their quality, such as picked Turkey, white Sennaar, Senegal, Cape, Mogador, Indian, Ghatti, Wattle, brown Barbary, &c. It is not necessary to enter into a very full description of all the varieties of gum arabic, as these are of little importance in connection with the topics dealt with in this book.

Picked Turkey or *white Sennaar arabic* is the produce of *Acacia Senegal*, a tree growing in the Upper Nile regions and in Kordofan, where it is collected by the natives and shipped to Egyptian ports for exportation. *Gum Senegal* is the produce of the same species of *Acacia*, and is collected in the French province of Senegal. This variety of gum is very varied in quality, ranging from a fine white gum to a dark somewhat reddish gum. It is exported from Senegal almost entirely to Bordeaux, and but little comes into England. The best qualities are used for pharmaceutical,

confectionery, and other purposes, while the common qualities find a use in textile industries, varnish-making, and for making mucilages. *Suakim* or *Soudan gum* is a variety of gum arabic derived from two other species of *Acacia*, *A. stenocarpa*, the talch or talha tree of the Arabs, and *A. Seyal*, the soffar tree of the natives. This variety is collected in the Upper Nile regions and in the districts through which some of its tributaries flow. It is sent into commerce either through Khartoum, or, more largely, through Suakim, a port on the Red Sea. Very large quantities of this gum come into the English market, and it forms the main source of the gum arabic used for general commercial purposes. Its quality varies somewhat, from a good fine white gum to a dark discoloured sort. *Morocco gum arabic* is said to come from *Acacia gummifera*, but its source is somewhat uncertain. It is only collected in small quantities, and is chiefly exported through Mogador. It occurs in large globular tears of a brownish tint, from which circumstance it is sometimes known as brown Barbary gum. *Cape gum*.—The doornboom, *Acacia horrida*, one of the commonest trees of South Africa, yields a large quantity of a brownish gum, which differs from gum arabic in not being so completely soluble in water. It is used in the Cape Colony and surrounding districts in place of gum arabic, and is exported to a small extent. *East Indian gum*.—Much of what is sold as East Indian gum arabic is African produce, exported by way of Aden and Bombay, and does not differ, therefore, from Suakim gum in quality. Several species of *Acacia* grow in India and yield gum, which is collected and used locally, but a little finds its way into this country. Not much is known about these Indian gums. The *Acacia arabica* grows in Bengal, the Deccan, and Coromandel. The *Acacia catechu*, the cutch tree, yields a gum of rather dark colour, but otherwise equal to gum arabic in quality. *Acacia speciosa* yields a gum, known in India as the siris gum, which is of good quality. From other Indian *Acacias* gums are obtained in smaller quantities. Besides the *Acacias* other trees yield gums which sometimes find their way into the English market, such, for example, as gum ghatti; these gums are not so good as true gum arabic. The gums from the Australian wattles (which are various species of *Acacia*, the principal tree being the green wattle) *A. decurrens*, *A. pycnantha*, *A. homalophylla*, *A. harpophylla*, and *A. Bidwilli*, are of smaller importance. The quantity of gum obtained is rather larger than from African trees, and is of good quality.

The following description is nearly applicable to all the above varieties of gums. Gum arabic occurs in roundish or ovoid or

even vermicular masses of various sizes; the surface always has a glistening appearance, the colour varies from an almost colourless gum to a faint reddish or brownish tinted gum. While some pieces are transparent, many are simply translucent, and some are opaque; they are brittle and easily friable, although this property is a variable one, the Australian gums being less friable than the others; gum Senegal is generally the most friable. These gums are quite free from odour, and their taste is slight. They are quite soluble in water; the best qualities take about $1\frac{1}{2}$ times their weight of water to form a thick viscid, highly adhesive mucilage, which is insoluble in alcohol; hence the addition of alcohol to the aqueous solution causes the precipitation of the gum. A solution of subacetate of lead added to the aqueous solution results in the formation of an opaque white jelly. Iodine does not produce any colour in solutions of gum arabic. Nitric acid converts them into mucic and oxalic acids; while boiling with sulphuric acid converts them into dextrine and sugar.

Gum arabic consists essentially of arabine, a compound of arabic acid ($C_{12}H_{22}O_{11}$) with lime; besides this compound gum contains traces of sugar, dextrine, colouring matter, tannin, and mineral matter.

Gum Tragacanth.—This gum is an exudation from various species of *Astragalus*, of which the most common is *A. gummifera*, growing in Lebanon, Syria, Central Asia Minor, and Armenia. Other species of *Astragalus* growing in Asia Minor, Judea, Syria, and Persia also yield gum tragacanth, which comes into commerce principally through Baghdad. Gum tragacanth occurs in two forms—(1) leaf gum, in strips of about $\frac{1}{2}$ to $\frac{3}{4}$ inch wide, and 2 to 3 inches long; (2) “vermicelli” gum, in long round pieces. It is of a dull greyish colour, without odour or taste. Placed in cold water it does not dissolve, but swells up into a gelatinous mass, which, when boiled for some considerable time, gradually passes into a kind of solution forming a very jelly-like fluid. It is readily soluble in alkaline liquids, but not in alcohol. It consists essentially of a compound known as bassorine ($C_6H_{10}O_5$), which is insoluble in water and alcohol. Besides this there is generally a small quantity of ordinary arabine soluble gum. Gum tragacanth, owing to its dull appearance, is not used in varnish making, but finds a use as a thickener in calico-printing, and for a few other purposes.

Besides these two gums, other kinds of gums are occasionally met with in small quantities in the London market. Some resemble gum arabic in their properties, and can be used for the same purposes; others resemble gum tragacanth; while some,

such as the kuteera gum of India, appear to contain both soluble and insoluble gums.

Dextrine or British Gum.—This product sometimes occurs in water varnishes. It is prepared by acting on starch either by heat alone or by heating with a small quantity of acid; the former method is most commonly used in England, and gives the best dextrine; the acid method is the one by which German dextrine is mostly prepared. Dextrine comes into commerce as a powder varying in colour from a pale yellow, "white," to a dark brownish-yellow, "yellow" dextrine; intermediate varieties being known as "canary." Pure dextrine is quite white, tasteless, and free from odour, the commercial varieties have a sweetish taste and slight odour. Pure dextrine is quite soluble in water; the solution reduces Fehling's solution and gives a brownish colour with iodine. The solubility of the commercial dextrines varies considerably; some are quite soluble, others are only partially soluble, as they still contain some unchanged starch. These solutions reduce Fehling's solution, and often give a blue colour with iodine. The solutions have more or less adhesive properties; hence, dextrine is largely used for adhesive purposes as a substitute for gum arabic. Dextrine dries with a fair amount of gloss or lustre; hence it is used in making water varnishes. There is a considerable difference in the commercial varieties of dextrine in regard to both their adhesive and lustreing properties, some, while giving a thick mucilage, have little adhesive property, and others dry with little gloss. On boiling with water, dextrine gradually loses its adhesive properties, which change is hastened by the addition of small quantities of acid; this is due to the transformation of the dextrine into sugar.

Gelatine.—This is an animal product obtained by boiling the cartilaginous tissues of animals, bones, &c., in water, and evaporating the solution down and drying the product. The character of the product varies very considerably according to the material from which it is extracted and the care with which the process of manufacture is carried out. The finer qualities known as gelatine are generally in the form of thin sheets of 7 or 8 inches in length by 2 or 3 inches in breadth; quite white, or rather colourless, and transparent sheets are flexible and tough, not being readily broken. The commoner qualities are known as glue, and vary very much in appearance; the better qualities are made in thin sheets of the same size as the gelatine sheets above mentioned, but a little thicker; they are of a pale yellowish-white colour; the inferior qualities are generally made in sheets of about 6 inches square of varying thickness and usually of a

reddish-brown colour, more or less transparent. Glue is valued on account of its adhesive properties and is used in many arts. Gelatine is used in making varnishes and for fine work, where a colourless adhesive is required. Gelatine when placed in cold water swells up into a jelly-like mass; when boiled with water it dissolves, forming a thick viscid solution having very strong adhesive properties; on cooling, this solution forms a jelly-like mass. It takes but a small proportion (from $\frac{1}{2}$ to 1 per cent.) of gelatine to cause a solution to set into a jelly on cooling. Spread over a surface gelatine dries with a fair amount of lustre. The dry surface is, however, sensitive to the action of water; but by mixing a small proportion of potassium chromate or bichromate, and afterwards exposing the surface to the action of light, the gelatine is rendered insoluble in water; by taking advantage of this property waterproof varnishes may be made from gelatine. It only requires about $\frac{1}{2}$ to 1 per cent. (of the weight of the gelatine) of the chromates to effect this change. Gelatine is insoluble in alcohol, and the addition of that body to an aqueous solution causes the precipitation of the gelatine in the form of a viscid adhesive mass. Tannin likewise precipitates gelatine from aqueous solutions as also do solutions of various gums. Gelatine solutions, if kept, decompose and evolve a putrid odour; this decomposition may be prevented by the addition of a few drops of some antiseptic, such as thymol, carbolic acid, salicylic acid, &c.

Albumen.—Albumen is obtained from the white of eggs or from blood-serum by a process of drying, when it forms horny masses of a pale yellow colour and high lustre. Egg albumen is the best of the two varieties, having a whitish colour and the highest lustre. Albumen is soluble in cold water; but ordinary commercial samples generally contain a small quantity of insoluble albumen, due to their being dried at rather too high a temperature. The characteristic property of albumen is that when the aqueous solutions are heated the albumen is coagulated and falls as a white insoluble mass; this property is exceedingly characteristic of albumen, and upon it much of its application in calico-printing, &c., is based. It is also precipitated from its solutions by various metallic salts and by alcohol. Its aqueous solutions are very liable to decompose, giving off small quantities of sulphuretted hydrogen, &c.; this decomposition may be prevented by the addition of antiseptics, as in the case of gelatine. Albumen occurs in some kinds of water varnishes which are almost entirely composed of it as it does not work well with other bodies.

4th. SOLVENTS.—These have already been sufficiently described (see pp. 360 to 383).

5th. DRIERS.—These also have been previously dealt with (see p. 386, *et seq.*). They are used in making oil varnishes for the same purpose as in paint making—*i.e.*, to make the varnish dry quicker. They should be used very sparingly, as they do not add to the durability of the varnish at all, their tendency being to make the coat harder, but more liable to crack, while they reduce the lustre and transparency.

6th. COLOURING MATTERS.—The materials which may be used in the manufacture of varnishes for the purpose of colouring them are very numerous, and the number has been much increased of late years by the introduction of the coal-tar colours. They may be divided into two groups:—1, Natural colouring matters, and 2, artificial colouring matters; the latter group is now by far the most numerous.

1. NATURAL COLOURING MATTERS.—There are a fairly large number of these bodies at the disposal of the varnish maker; but he cannot use all the colouring matters which may, or can, be obtained from natural sources, as one important property which varnish colours must possess, *viz.*, solubility in oil and spirit, is not possessed by many, as, for example, indigo, hæmatoxylin, and the colouring matter of logwood. The following products can be used for colouring varnishes:—

Turmeric.—This natural yellow dyestuff is the rhizome or root-stem of several species of *Curcuma*; *C. longa*, *C. tinctoria*, and *C. rotunda* being those which yield the largest portion of the turmeric of commerce. They are found in many parts of Asia, but the principal supply comes from Bengal and Madras in India; some comes from China, Siam, and Singapore. Turmeric is usually sold in the form of root-shaped masses, some varieties being more or less branched; these are externally of a greyish and internally of a deep orange-yellow colour; in taste they are somewhat bitter and hot. The colouring matter is but slightly soluble in cold, but more freely soluble in hot water. Alcohol dissolves the colouring matter from turmeric as well as some resinous matter. An analysis of turmeric root shows it to contain 11 to 12 per cent. of colouring matter, 10 to 11 per cent. of a yellow-brown resin, 1 per cent. of a volatile oil, 14 per cent. of gummy matter, 57 per cent. of starch, soluble salts, &c., and about 7 per cent. of water.

The colouring principle of turmeric is called curcumin, a body having the formula $C_{14}H_{14}O_4$. It can be obtained from turmeric by digesting the powdered root with water until no more colour is extracted, evaporating down the solution to dryness, extracting with benzene and purifying by crystallisation from alcohol. Other methods for extracting it can be adopted. Curcumin crystallises

from hot alcohol in needle-shaped prisms, having an orange-red colour with a blue reflection, is odourless, and melts at 178°C . It is slightly soluble in water, but more readily soluble in alcohol, especially when boiling; it is also soluble in wood spirit and in glacial acetic acid; it is practically insoluble in petroleum ether. Strong sulphuric acid dissolves it; at first the solution has a reddish purple colour, but this soon changes to black owing to charring taking place. In solutions of alkalies, either the caustic or carbonate, curcumin dissolves with a reddish-brown colour. Curcumin is very sensitive to alkalies, and hence is often used as a test for alkalinity, the merest trace of alkali being sufficient to turn a solution of turmeric from yellow to brown.

A very characteristic reaction for turmeric and its colouring principle, curcumin, is the red colour which it gives with boric acid, which colour is quite distinct from that given by alkalies. This colour is produced when an aqueous solution of boric acid is added to an aqueous solution of turmeric. A solution of borax, to which hydrochloric acid has been added in sufficient amount as to make the solution acid to litmus, may be used instead of the boric acid. Paper coloured with turmeric tincture, dried, and then moistened with the acidified solution of borax, shows this reaction very well, but still better if it be again dried.

Turmeric root is rarely adulterated, but the turmeric powder is sometimes mixed with starch and mineral matters. The latter can be detected by the increase in the amount of ash left on burning; this ash should not be more than 5 per cent., and an analysis of it will soon show whether any mineral matter has been added. Starch is best detected by the microscope and by the fact that its addition materially reduces the proportion of ash and increases the proportion of soluble matter.

Turmeric is used to give a yellow colour to varnishes and stains, which stain is tolerably permanent.

Gamboge.—Gamboge is a gum-resin, the product of *Garcinia morella*, a tree growing in Siam, from whence gamboge is exported in large quantities. It usually occurs in cylindrical rolls of about an inch or an inch and a quarter in diameter, and of varying length; these rolls, which are of an orange colour externally, are made by melting the gum-resin, and pouring the melted material into moulds made of bamboo cane. It is rather brittle, and the pieces of gamboge are often covered with a yellow powder. When broken it exhibits a conchoidal fracture with a vitreous lustre. When viewed through the edges it is more or less transparent. Its solution in water is rather cloudy, and of a yellow colour; its taste is but slight at first, but an

acid after-taste is perceived. It possesses strong purgative properties, and, hence, is frequently used in medicine.

An analysis made by the author shows it to contain—

Moisture,	2.50 per cent.
Mineral matter,	1.05 „
Resin, soluble in ether,	66.05 „
Wax, soluble in alcohol,	4.31 „
Gum,	26.03 „
	<hr/>
	99.94

Gambogin, or gambogic acid, the resin of gamboge has, according to Buchner, the formula $C_{30}H_{35}O_6$. It is obtained in a rather impure condition by treating gamboge with ether; on evaporating off the ether the gambogin is left behind as a transparent, vitreous, and brittle mass, breaking with a conchoidal fracture. In colour it is a reddish-orange, forming a yellow powder. When heated it softens, and melts at about 75° to 80° C.; on cooling, the mass again becomes solid. It has no odour nor taste, and is destitute of purgative properties. Gamboge resin is readily soluble in ether, alcohol, and chloroform; petroleum spirit has but a slight solvent action on it. It readily dissolves in alkaline solutions. The carbonates of the alkalis are decomposed by it on boiling, with evolution of carbonic acid, showing that it has acid properties. The solutions have an orange-red colour; when acidulated they deposit the resin in flakes.

The wax, which is insoluble in ether, but soluble in alcohol, is a soft brownish substance, melting readily at a low temperature; it has a bitter taste, which is very persistent, and a slight purgative action. Caustic soda dissolves it with a brownish-yellow colour; the addition of acids reprecipitates it.

The gum is a transparent brownish mass, having a sweet taste, and but slightly adhesive properties. It dissolves in water, forming a somewhat opalescent solution, which, on adding an acid, becomes clear. It is not precipitated by basic lead acetate, mercuric chloride, ferric chloride, borax, or alcohol. It seems to be a glucoside, yielding a sugar on hydrolysis.

Gamboge is soluble in alcohol, partially in ether, readily in ammonia. It is used as a pigment in water-colour painting, and also for colouring varnishes.

Dragon's Blood.—This is a product of *Calamus draco*, the tree which yields the rattan canes of commerce, and a native of Eastern Asia, from which country this resin is sent in large quantities to Europe. The fruit of this tree, on approaching

maturity, becomes covered with a red resinous mass of a friable character; this resin is collected by shaking the fruits into baskets, and then sifting the resin from the stems and particles of woody fibre. The resin is then melted either by the heat of the sun, or by that of boiling water, and cast into rolls by wrapping it in a palm leaf; in this form it is sent into commerce, being exported into this country from Singapore, Batavia, and other Asiatic ports. Dragon's blood occurs in the form of roughly cylindrical sticks about 13 to 14 inches long, and about $\frac{3}{4}$ to 1 inch thick; but smaller pieces are by no means uncommon. Externally, the resin has a blackish-brown colour; but viewed in thin slices it is transparent, and of a deep crimson colour. Its specific gravity is about 1.2, varying a little, the best qualities always having the highest specific gravity. Its taste is sweet when pure, but adulterated samples often have an acrid taste.

It is soluble in alcohol, benzol, chloroform, carbon bisulphide, petroleum spirit, shale spirit, glacial acetic acid, caustic soda, and some other solvents; it is only slightly soluble in ether, and is all but insoluble in turpentine. It melts at about 120° C. (248° F.), and when heated evolves benzoic acid. It is used for colouring spirit varnishes a deep red, and for this purpose is one of the best colouring matters which can be used.

Besides the above, a few other varieties of dragon's blood are met with in commerce to a small extent. *Socotran dragon's blood*, the resin of the *Dracæna Ombet* or of *D. schizantha*, from which trees the natives obtain the resin by making incisions in the bark and collecting the resin which exudes. This variety comes into the London market from Bombay and Zanzibar in the form of drops or tears. An exactly similar product is obtained in the Somali country.

Canary Islands dragon's blood is the variety obtained from the celebrated dragon tree of Teneriffe and adjacent islands, *Dracæna draco*. Very little of this now finds its way into European commerce, but it is used locally for various purposes. *Mexican dragon's blood* is obtained from *Croton draco*, but is rarely met with in English commerce.

Gum Accroides, also known as black-boy gum, *Xanthorrhæa* resin, &c. The resins yielded by the several species of *Xanthorrhæa*, natives of Australia, have of late years been imported to a large amount for varnish making. Some six or seven species of *Xanthorrhæa* are known to yield resin in large amount; in the season the resin exudes in no inconsiderable amount, but by crushing the stems and sifting further quantities are obtained. The prin-

cipal species are *Xanthorrhœa australis*, which grows in parts of Victoria, *X. hastilis* and *X. arborea*. The resin is distinguished as red or yellow; by some authorities these have been ascribed to different trees; on the other hand, it is possible that the red may simply be derived from the yellow by exposure to the air. All the varieties of gum accroides are soluble in alcohol with a strong yellow colour. The odour is pleasant, and resembles that of benzoin. Treated with nitric acid it yields a large proportion of picric acid. Its specific gravity is 1.197.

2. COAL-TAR COLOURS.—This is a very large and varied group of colouring matters, many of which have come largely into use during late years for colouring varnishes and making the so-called enamel paints. It is not necessary to deal with the chemical nature of these colouring matters here, the reader is, therefore, referred to the author's *Dictionary of Coal-tar Colours*, or to Benedikt & Knecht's *Chemistry of Coal-tar Colours*, for details on this subject.

The coal-tar colours can be divided into four groups:—

1. *The Benzidine colours*, whose characteristic feature is that they will dye unmordanted cotton from a boiling bath of salt or other alkaline compound. As a rule, this class of colours, which includes Congo red, benzopurpurine, chrysamine, benzoazurine, Titan pink, Titan yellow, diamine-yellows, &c., are of no use as colouring agents in varnish making, as their solubility in alcohol, oil, and other varnish solvents is but slight; not only so, but many of them, the reds especially, are rather fugitive to light, and are readily acted upon by any substance having weak acid properties.

2. *Basic Colouring Matters.*—This is a numerous group of colouring matters, many of which are of great use in varnish making. The group includes magenta, safranine, Bismarck-brown, chrysoidine, phosphine, rhodamine, chinoline-yellow, auramine, induline, nigrosine, soluble blue, methyl-violet, Hofmann violet, benzyl violet, brilliant green, methyl-green, &c. All these colours are soluble in water and in alcohol. They can, therefore, be used for colouring water- or spirit-varnishes. Magenta gives crimsons, but should be used in comparatively dilute solutions, say of a strength of about 1 per cent., as when stronger the solutions are apt on drying to leave a bronzy colour behind, and not a red. Safranine can be used for scarlets, especially if mixed with a little auramine. Phosphine can be used for oranges, but it is rather expensive. Rhodamine can be used for pink varnishes. Auramine dyes yellows. Induline, nigrosine, and another product generally known as brilliant black, belong to a peculiar group of dyestuffs which exist in two forms; one, soluble in water and

almost insoluble in spirit; the other, insoluble in water, but soluble in spirit; this latter variety is distinguished as induline spirit soluble, or nigrosine spirit soluble, as the case may be. Brilliant black is only made in the spirit soluble form. These dyes are very useful to the varnish maker. Induline gives dark blues; there are several brands of induline giving various shades of blues. Nigrosine can be used for greys, and when used in large proportion gives very good blacks. Brilliant black gives blacks; these, like induline, are made in various brands, giving different shades of greys and blacks, some bluish, others greyish in tone; a varnish maker should obtain samples from various makers, and use that which gives him the best results as to strength of colour and tone. The other colouring matters named above are sufficiently indicated by their name; the violets are made in several shades, from a red to a blue-violet; like magenta, they should not be used in too strong a solution or they dry up with a bronzy cast; the greens are of a blue shade, but by mixing them with a yellow, a pure green or a variety of different shades, from a blue- to a yellow-green, can be readily obtained.

These colouring matters do not readily dissolve in oil or oil varnishes, to which they give, as a rule, but a faint coloration, but the bases of these basic dyestuffs are soluble in oil without much difficulty; these bases are made on a limited scale by Messrs. Read Holliday & Sons, and other makers, and sold under the name of oil-yellow, oil-scarlet, oil-green, &c., expressly for the purpose of colouring oils and fatty matters in general.

3. *Acid Colouring Matters*.—This group of dyestuffs is characterised by its dyeing wool and silk direct in an acid bath; hence the name "acid" colours. It is divisible into several sub-groups depending upon the chemical composition and relations of the dyes, viz. :—

a. The *Eosins*, a class of colouring matter derived from fluorescein and characterised by giving scarlets of various hues of a very bright character; they are, however, rather fugitive. They are readily soluble in water and alcohol, and their solutions have a fluorescence of a more or less pronounced character. Eosin G has a yellowish-green, and erythrosine a trifling fluorescence; safrosin, faint yellowish-green; phloxine, light green; rose Bengal has no fluorescence in an aqueous solution, but an alcoholic solution has a golden yellow fluorescence; erythrin, green-yellow; eosin J, strong green-yellow; cyanosin, orange-yellow; chrysolin, yellowish-green; the fluorescence is in each case strongest in the alcoholic solution. Although the eosins can be used for colouring spirit varnishes, yet they are not satisfactory in use, as they have a tendency to dry with a yellowish bloom or fluorescence, which

obscures their real colour. The eosins are sold under a variety of other names.

b. Nitro-colouring matters, such as naphthol-yellow, aurantia, picric acid, citronine, &c., which are more or less of a yellow or orange colour, and are generally soluble in water and spirit; they are fairly permanent and can be used with advantage in the colouring of varnishes.

c. Acid colouring matters, such as acid magenta, acid green, acid yellow, acid violet, &c., which are mostly derivatives of the basic colours made by the process of sulphonation; they are readily soluble in water, but not all are soluble in spirit. They can be used for colouring varnishes.

d. Azo-colours.—This is a very numerous group of coal-tar dyestuffs mostly of a red, orange, or yellow colour, very few azo-blues, greens, or violets being known. The scarlets, croceine scarlets, ponceaus, azo-yellow, azo-violets, oranges, naphthol blacks and green, and most of the new blacks belong to this group of dyestuffs. The azo-dyes are, however, too numerous to give a detailed list of their names. These colouring matters are nearly all soluble in water; some are soluble in spirit, as shown in the list given below, and may be used for colouring varnishes, since, as a rule, they give very bright colours possessing a fair degree of fastness on exposure to light and air.

4. Adjective Dyestuffs.—This class of colouring matters is characterised by the members requiring the aid of a second substance, the mordant, to fix them on the fibre and to develop the colour from the dyestuff. It includes alizarine and all the so-called alizarine dyes, gambine, coerulein, gallein, gallocyanine, galloflavine, &c. As colouring matters for varnishes they are quite useless, as they do not possess, as a rule, the essential feature of being soluble in water or spirit.

The following tables of the solubility of the coal-tar colours in various media will be found very useful by the varnish maker as showing him what can and what cannot be used for colouring varnishes:—

1. *Colouring matters soluble in water and alcohol.*

Magenta.	Acid magenta.	Vesuvine.	Iodine green.
Cardinal.	Cerise.	Rubin.	Crimson.
Erythrosin.	Rose Bengal.	Methyl eosin.	Eosin.
Safranine.	Cocaine.	Phloxine,	Corallin.
Methylene blue.	Peacock blue.	Navy blue.	Benzyl blue.
Picric acid.	Naphthol yellow.	Phosphine.	Aurantia.
Curcumine.	Brilliant yellow.	Auramine.	Chrysophenine.
Metanil yellow.	Methyl orange.	Chrysoidine.	Mandarin.
Hofmann violet.	Regina purple.	Methyl violet.	Acid violet.
Malachite green.	Brilliant green.	Acid mauve.	Methyl green.
Bismarck brown.			

2. *Colouring matters soluble in water only.*

Congo.	Heliotrope.	China blue.	Brilliant scarlet.
Congo corinth.	Brilliant blue.	Regina violet.	Acid yellow.
Brilliant Congo.	Wool blue.	Azo-violet.	Resorcin yellow.
Benzopurpurine.	Black blue.	Fast brown.	Quinoline yellow.
Delta purpurine.	Benzoazurine.	Acid brown.	Azo-acid yellow.
Roseazurine.	Azo-blue.	Resorcin brown.	Naphthol yellow.
Hessian purple.	Guernsey blue.	Guinea green.	Chrysamine.
Fast red.	Hessian blue.	Aniline grey.	Hessian yellow.
Archil red.	Water blue.	Nigrosine.	Curcumein.
Ponceau.	Bavarian blue.	Silver grey.	Orange.
Scarlet.	Capri blue.	Wool black.	Methyl orange.
Azo-rubine.	Alkali blue.	Nacarat.	Rubin S.

3. *Colouring matters soluble in alcohol only.*

Rosaniline base.	Aurine.	Soudan.	Spirit blue.
Nigrosine spirit soluble.	Malachite green base.	Brilliant black.	Induline spirit soluble.
Humboldt blue.	New violet.	Auramine base.	

4. *Colours soluble in oil.*

Rosaniline base.	Violet base.	Soudan I.	Soudan II.
Magenta base.	Auramine base.	Picric acid.	Oil green.
Oil yellow.	Oil violet.	Oil orange.	Oil crimson.
Butter yellow.	Oil brown.	Oil scarlet.	

Practically none of the coal-tar colours are soluble in petroleum spirit, turpentine, or benzol. While, therefore, the coal-tar colours are available for colouring water- and spirit-varnishes, but few of them are useful for colouring oil-varnishes, and none for colouring varnishes made from turpentine, petroleum spirit, or benzol.

VARNISH MAKING.

For practical purposes the following simple classification into four groups is quite sufficient:—

- 1st. Natural varnishes.
- 2nd. Oil varnishes.
- 3rd. Spirit varnishes.
- 4th. Water varnishes.

The first group comprises the natural lacquers of India, China and Japan, which issue from the tree in a liquid form, and only require applying to the prepared object to varnish them. The second group consists of the artificial varnishes made from resins of various kinds dissolved in oil; these form very useful varnishes

and are applied to all kinds of objects. The third group includes the varnishes made by dissolving resins of volatile spirits of various kinds; on application to the object the spirit evaporates and leaves the resin behind as a lustrous coat. The fourth group embraces a few varnishes made by dissolving resins and gums in water; they are not numerous and are only used for special purposes.

1st. NATURAL VARNISHES.

In India, China, and Japan are found a number of trees of various species whose sap or juice has the property of drying hard with some considerable lustre; the sap is collected and used for a varnish in the countries named; none of it is exported to this country. The natural varnish of Japan is the variety best known in this country; it is used for producing the famous lacquer ware of the Eastern Empire.

1. **Japan Lacquer.**—The best account of this material has been published in the form of a Consulate Report by Mr. John J. Quinn, the acting Consul at Hakodate,⁵ 1882, on the "Lacquer Industry of Japan," from which the following brief description has been taken:—

The Japanese lacquer is the product of the *Rhus vernicifera*, a tree found growing all over the main island and, in smaller quantity, in the other islands of the Japanese group. The lacquer trees are cultivated, and some companies have been formed to plant waste lands with the trees; they may be grown from seed sown about February, the young trees being transplanted when about a year old.

It takes ten years to raise a tree from seed to the lacquer yielding state, and even then it only gives about 3 ozs.; by grafting, the trees can be made to grow quicker, and then a ten-year old tree will yield about 4½ ozs. of lacquer. There are some differences in the quality of the lacquer yielded by trees grown in different localities; that coming from Tsugaru, Nambu, Akita, and Aizu is the best and most transparent, and is the variety most in use in Kyoto and Osaka, which are the great centres of the lacquer-ware industry.

In June of each year tappers go round the plantations, and, after certain preliminary operations, such as clearing the ground and marking the trees, makes a number of cuts on the trees; from each of these cuts sap exudes and is collected. The quality of the sap obtained from the cuts varies somewhat; that from the

first five cuts is poor, containing a good deal of water; that from the middle fifteen cuts is the best; that from the last five cuts is thin. As a rule the tapping of the tree kills it, although, by not giving quite so many cuts, a second year's flow of sap can be obtained, but such sap is not so good as the first year's sap, so that a tree is rarely tapped twice. The custom is for the lacquer merchants to buy the right of tapping the trees from the farmers; the latter still keeping possession of the tree, and when it has been tapped generally cut it down for firewood or for making cabinet ware, &c.

The lacquer obtained from the trees is known as *Ki-urushi* or tree lacquer, and *Seshime* or branch lacquer, these terms indicating from which part of the tree the lacquer comes. The lacquer merchants buy this lacquer from the tappers, and then treat it in various ways for sale to the lacquer-ware makers. The crude lacquer contains some water, and in preparing it for use this water has to be eliminated, which is done by allowing the lacquer to stand in vessels exposed to the rays of the sun for some time; the operation is facilitated by adding a small quantity of water to the crude lacquer.

Crude lacquer is a liquid of about the colour and the consistence of cream; if exposed to the sun for some days it loses its colour and becomes quite black or nearly so, but at the same time becomes more or less transparent, and will not dry when used for lacquering articles; if, however, some water be mixed with it two or three times a day for two or three days, and this extra water be evaporated away in the usual manner, then the lacquer acquires the property of drying and may be used for lacquering. Branch lacquer does not dry so quickly as tree lacquer, and is, therefore, rarely used alone; thence mixtures of the lacquer are made with other ingredients and sold under a variety of names for special kinds of lacquer ware.

Old lacquer is more difficult to treat than new lacquer. One of the most peculiar properties of Japan lacquer is that it will not dry in a dry atmosphere, but it requires a damp one to become hard.

As might be expected the lacquer varies in composition; this may arise partly from natural causes and partly from the fact that the lacquer merchants rarely sell the lacquer in the same condition as they obtain it, but generally mix it with other bodies. Two analyses of Japanese lacquers have been published. Mr. S. Isima Ishimatsu gives the following as the composition of a sample of *Yoshino* lacquer, which is one of the best varieties:—

The specific gravity at 20° C. was 1.002 and it contained—

Urushic acid,	85.15 per cent.
Gum arabic,	3.15 ,,
Nitrogenous matter,	2.28 ,,
Water and volatile matter,	9.42 ,,

Another sample analysed by Mr. J. Takayma had the composition—

Urushic acid,	64.07 per cent.
Gum arabic,	6.05 ,,
Nitrogenous matter,	3.43 ,,
Oil,	0.23 ,,
Water and volatile matter,	26.22 ,,

The higher the proportion of urushic acid contained in the lacquer, the better is the quality of the article. Urushic acid contains 77.05 per cent. of carbon, 9.01 hydrogen, and 13.94 oxygen, corresponding to the formula $C_{22}H_{31}O_3$.

Chinese lacquer is identical with Japanese lacquer. China, indeed, is the home of the lacquer industry, from whence it spread to Japan, where it has become of more importance than in its original home.

Indian and Ceylon Lacquer.—From several trees, natives of India and Ceylon, is obtained the natural varnish used by Indian and Cingalese artificers in the manufacture of lacquer ware. In Ceylon the lacquer comes from a species of *Semecarpus*, which grows tolerably luxuriantly all over the island. In India several trees yield the lacquer, viz., *Semecarpus anacardium*, which grows in the Concan, Coromandel, Courtallum, Gujerat, Bengal, and Travancore districts; and *Semecarpus travancorica*, which grows in the damp forests of the Travancore and Tinnevely mountains. In the Western Ghauts of Madras and Bombay and in Bengal lacquer is obtained from *Holigarna longifolia*, which exudes the juice from fissures in the bark; while in *Semecarpus* it comes from the pericarp. After exuding from the tree it is collected and sold to the lacquer-ware makers; it readily hardens on exposure and assumes a black colour in so doing; as a varnish it is very good, being lustrous, transparent, hard, and strongly adhesive.

Burmese Lacquer.—This lacquer, which is used in large quantities in the preparation of Burmese lacquer ware of all kinds, is obtained from every part of the kheu tree, *Melanorrhœa usitatissima*, which grows very abundantly in every part of the country, but more particularly in the Kubbu valley where it attains its greatest size; on the sea coast it is usually of somewhat dwarfish growth. The varnish is collected during January to

April. The collector makes wounds in the bark of the tree and thrusts into them short lengths of bamboo, in which the juice collects; as the bamboos get filled they are emptied and replaced; there will often be as many as 100 bamboo canes in a single tree, the usual yield of which is about $3\frac{1}{2}$ lbs. of lacquer. Burmese lacquer is a thick, very viscid liquid having a turpentinous odour; in colour it is grey, but on exposure it soon becomes black. It dissolves freely in alcohol, benzene, and turpentine. It dries hard and lustrous, but rather slowly. Its drying is facilitated by mixing a little gold size or other varnish with it. Gingelly oil is often added to the lacquer.

2nd. MANUFACTURE OF OIL VARNISHES.

Oil varnishes are divided commercially into two groups, coach varnishes and cabinet varnishes, although there is very little difference between them in either the method of making, or the materials from which they are made. The former are the best and most durable varnishes made, the best materials and workmanship being employed, while less care is taken with cabinet varnishes. The process of manufacture is, however, the same for all the oil varnishes. The materials used are resins of various kinds, linseed oil (rarely any other kind of oil), turpentine, shale-, petroleum-, or rosin-spirit, and, for some special sorts of varnish, other ingredients. The process usually adopted for their manufacture will be first pointed out; then any special process which is or has been used; then important points of detail in the process will be noticed, and recipes given for various kinds of oil varnishes, followed by a section dealing with their general properties, application, &c.

MANUFACTURE OF OIL VARNISHES.—The method and plant used in the manufacture of this class of varnishes are comparatively simple, but the process itself, while being so simple, is one that requires very great care and experience to carry out to a successful end.

The process in outline consists of the following stages:—1st, Melting (or “running,” as it is known in the trade) the resin or “gum”; 2nd, boiling the oil; 3rd, mixing the melted gum and boiling oil; 4th, boiling the varnish; 5th, thinning the boiled varnish; 6th, clearing.

1st, “**Gum Running.**”—This is perhaps the most delicate operation in the whole process of varnish making, as unless it is well done good varnish cannot be made, no matter how well the

rest of the process be carried out. "Running" is done in a large cylindrical copper vessel, the "gum pot"; there are two forms of this gum pot in use, one, known as the London pot, is shaped like a silk hat (Fig. 65), and is made in two pieces—viz., the bottom formed of a solid piece of cast copper with a flange

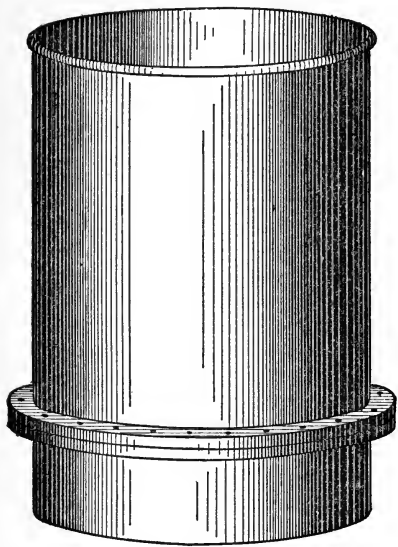


Fig. 65.—Gum melting pot.

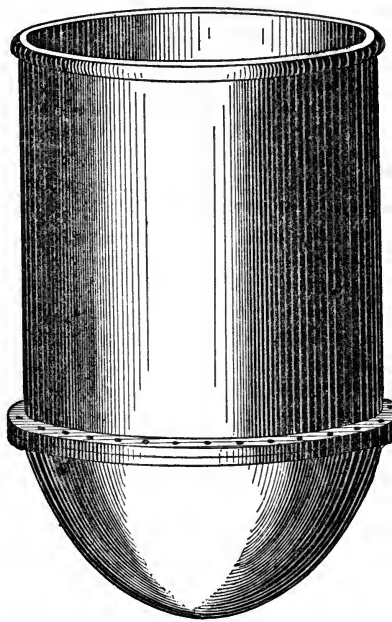


Fig. 66.—Gum melting pot.

cast on it; and the body, which is a cylinder of sheet copper, rivetted to the bottom piece. There is a very considerable wear of the bottom part, as it comes in contact with the fire, and hence has to be replaced from time to time; usually a bottom will last about three months. The gum pot usually measures about 26 inches in depth by 10 inches in diameter, the body being about 9 inches deep. This is large enough to run about 8 lbs. of gum at one time, but the pots are often made large enough to hold 50 lbs. of gum. In the north of England the gum pot is made of a different shape, as shown in Fig. 66, from which it will be seen that it differs principally in the shape of

the bottom, which is made conical. The main advantage of this form lies in the fact that the gum runner can more readily ascertain when the whole of the gum has been melted by probing with his stirrer; in the London shape particles of unmelted gum may lodge in the bottom corners, into which it is difficult to work the stirrer, whereas in the Northern shape any unmelted

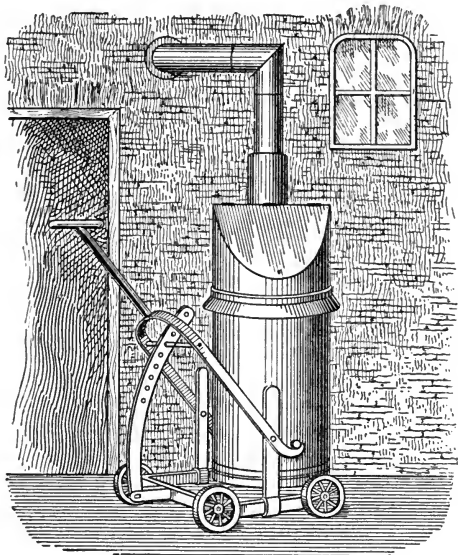


Fig. 67.

gum must settle down to the point of the conical bottom, and its presence there is easily ascertained. The "gum pot" rests by its flange in a suitable hole in the top of a furnace. In modern varnish works the top of the furnace forms the floor of the gum running shed, the furnaces themselves being fed with fuel from the outside, Fig. 67. The pots are also fitted to a pair of wheels, by which they can be wheeled from the gum running shed to the mixing shed; sometimes rails are laid, on which the pots are run. As a very considerable quantity of vapour of rather an acrid character is given off during the process of gum running, it is necessary to fit the pots with a hood connected with a flue, by which means all the vapours are carried into a chimney, and so away out into the atmosphere. It would be better, however, to

take the vapours into a large condensing chamber to allow as much as possible of them to condense into a liquid form, for which some uses (if only as fuel for the furnaces) could be found. This would prevent a considerable amount of nuisance being generated during the process of varnish making. In some large places where they have steam boilers the vapour is carried by means of a pipe to the ash-hole of the fire-place, and thus passed through the fire; the mouth of the pipe must be covered with wire gauze. Prior to the gum being run, it is broken up into small pieces about the size of a walnut. At one time this used to be done by hand with a hammer, but is now effected by a machine known as the breaker, usually consisting of a pair of rollers fitted with teeth, by which the gum is broken up as it passes between the rollers.

2nd, Oil Boiling.—While the gum is being “run” the oil to be used is boiled. This is done in what is known as the boiling pot, which is the same in shape as the oil boiling pots described when dealing with the boiling of linseed oil. The oil is heated to about 500° F. for 1 to 2 hours, when it is ready for mixing with the melted gum. The boiling of the oil is a comparatively simple operation, and there should be no difficulty in carrying it out.

3rd, Mixing.—When the gum has been properly run by being heated in the gum pot until it is in a quiet state of ebullition, and there is no more frothing; which always occurs when a gum is first heated, and which is a source of trouble in the operation of gum running by causing the gum to boil over and to become a source of danger by being liable to take fire if it finds its way into the furnace, as well as being a loss to the varnish maker. This frothing is probably due to the water which the resin naturally contains being driven off, as well as to the escape of the more volatile constituents of the resin; when this frothing happens the best thing to be done is to lift the pot from the fire and beat down the froth as much as possible; when it has subsided, the pot may be replaced on the fire and the gum again heated, these proceedings being repeated until all frothing ceases. With the object of preventing accidents from boiling over the gum pot is made deep, and to hold a much larger quantity of gum than is run at one time.

When the runner considers that the gum has been properly melted (on which point experience is the only reliable guide) the necessary quantity of the boiling oil is taken from the boiling pot in the copper jack and poured into the melted gum, which is stirred energetically all the time. When properly mixed the

contents of the gum pot are poured into the set pot (see below); the gum pot is then ready for another run of gum. What has here been described is called a "run;" usually a large number of runs are made and put into the set pot for treatment at one time by the next operation.

In the early days of varnish making the usual quantity of gum run at one time was 8 lbs., and all recipes for making varnish are based on this figure; but nowadays quantities of 50 or 60 lbs. are commonly run at one time.

4th, Boiling.—For the purpose of boiling the mixture of oil and gum so as to cause them to combine together properly and to increase their drying properties, what is called a "set pot" is used. This is an iron vessel, in shape resembling a washing boiler, having a capacity of about 600 gallons, and set in a suitably constructed furnace. Several runs of gum are poured into it, and the whole heated or boiled at from 450° to 500° F. The duration of the boil varies with different kinds of varnish, and may range from half an hour to 4 or 5 hours. When sufficiently boiled the liquid has a certain amount of stringiness. When the gum and oil are first mixed they will not string—that is, if a drop be taken between the finger and thumb, and these be extended, the varnish will not extend in the form of strings; by boiling it obtains this property, and the longer it is boiled the more extensible does it become; some varnishes only require a moderate amount of stringiness, others require a great deal; instructions on this point will be given when dealing with each individual varnish. Another effect of the boiling is to make the varnish clear and transparent; the mixture of gum and oil when first made is usually rather cloudy, but clears up on boiling.

The set pot should be so placed in the furnace that it can be readily lifted out at the end of the boiling, and be taken out of doors away from the proximity of the furnaces for the next operation. As a further precaution, a shallow concave cover filled with sand should be slung by chains over the pot. Should the oil take fire during the operation of boiling, this cover is quickly lowered down on to the pot and the fire smothered out before it has taken too great a hold of the oily mass. Water is perfectly useless for this purpose, and should never be used to put out burning oil; there is nothing better for this purpose than sand. Varnish making is always subject to the danger of the material firing; hence every precaution should be taken to have means at hand to provide the promptest extinction of the flames. It would be advisable to have the floor of the running and boiling shops made of sand, so that if any oil does boil over it will be absorbed

by the sand and would not inflame. A heap of sand should always be kept in a convenient position, so that it may be thrown on any oil that may by chance boil over. The fireplace should be so built as to be fed from the outside.

5th, Thinning.—After the boiling operation described above is completed, the set pot and its contents are removed from the fire and taken out of doors, if the weather permits, or into a shed specially used for this purpose, and which is at some distance from any fire; here it is mixed with turps, to thin it down to a working consistency. Turps is so volatile a body that if poured at once into the hot varnish mass it would be almost entirely driven off as a vapour, which is readily inflammable by contact with a fire or light. This thinning operation should, therefore, always be done at some considerable distance from a fire or light. Turps vapour, being heavy, travels along the ground, and may even reach a fire 20 feet away. Although it is necessary to mix the turps with the varnish mass at as high a temperature as possible, yet it is advisable to allow the hot varnish mass to cool down somewhat before adding the turps; this should also be added in small quantities at a time, and each lot well stirred in before adding the next lot; by these means the mixing will be properly done without too great a loss of turps.

6th, Clearing and Ageing.—Freshly-made varnish is most unsatisfactory to use, and all the best qualities are subjected to an ageing and clearing process before they are sent out. This process consists simply in putting them into large iron tanks or cisterns, where the varnish is kept (free from exposure to the atmosphere) for periods varying from six months to one and a-half or two years. During this time the particles of insoluble matter fall down, and the constituents becoming more thoroughly amalgamated, a clearer, more transparent, lustrous and more easily worked varnish is obtained.

Such is a brief description of the usual method of making oil varnishes. The quality of the varnish made depends upon a number of factors. The gum must be good and as free as possible from particles of vegetable matter, which, in the running, are apt to char and thus discolour the resulting varnish. For pale varnishes, clear, pale gums must be used; and the running must be both thorough and carefully done since there is no remedy for any defect due to a bad run, while one such run will spoil a whole batch of varnish. It should always be borne in mind that any gum left unmelted will not dissolve on adding the oil. Again, the temperature of running should not be too low nor too high; the former influences the bloom of the varnish, while

the latter tends to make the varnish too dark. The boiled oil should be hot, about 500° to 550° F., so that on being poured into the melted gum it will mix freely and not cool down the latter too much; after mixing it is advisable to boil the mixture for about ten minutes before pouring it out into the set pot. The best practical guide to all these and other points in varnish making is experience. The linseed oil used should be of the very best quality, as good varnish cannot be made from poor oil, and it ought to be kept in covered tanks for some months before using. The turps should also be of good quality; it is improved by keeping.

Another method of making varnishes, which was much advocated by Tingry, is to melt the gum in the usual way; then to run it out on to a cold surface so that it would solidify in sheets; when cold, the solid gum is roughly powdered, put into the boiling pot with the oil and boiled up as described above. In mixing, 3 lbs. of melted gum should be reckoned as equal to 4 lbs. of fresh gum; in other respects the same quantities of oil, &c., may be taken. The varnishes made by this method cannot be distinguished from those made by the old method. Tingry advised keeping the gum melted until it had lost 25 per cent. of its weight, and he devised a special form of melting apparatus by which this could be done; but the process was (for several reasons) a rather unpractical one.

It is stated in many accounts of varnish making that oil varnishes may be made by boiling the gum in the oil. As a general rule, this is not correct. A few gums may be dissolved in this way, but most of the oil varnish gums obstinately refuse to be transformed into varnishes by this method.

RECIPES.—Oil varnishes are divided by the trade into coach varnishes and cabinet varnishes, but there is no essential difference between them; they are made in the same way and often from the same materials; the difference is due to the carriage varnishes being made from better qualities of gums and oil and a little more care being taken in their preparation. The following recipes are taken from the most reliable sources and give particulars for preparing all the varieties of oil varnishes now in use. The preparation of varnishes is considered a trade secret, and it is difficult to obtain reliable information on the subject. What is here given and what is to be found in most accounts is based on a lecture on varnish making given by Mr. J. Wilson Neil to the Society of Arts many years ago, and published in an early volume of their Transactions, which is difficult to obtain now.

The proportions are generally given as for a run of 8 lbs. of gum.

1. Finishing Body Varnish for Coaches.—Run 8 lbs. of the best African animi, pour in 2 gallons of the best oil well boiled, set very slowly (by boiling for 4 to 5 hours until it strings well), allow to cool and add $3\frac{1}{2}$ gallons of turps; strain and allow to age. This varnish is considered to be the best varnish made, but it requires considerable care in making it to obtain it of good quality; the best and palest gum and the best oil must be used.

2. Hard Drying or Flatting Varnish.—This is made by running 8 lbs. of gum animi, mixing with 2 gallons of oil, and, after boiling for 4 hours, thinning with $3\frac{1}{2}$ gallons of turps.

This varnish dries rather harder than the above and quicker—*i.e.*, in about 8 to 10 hours. It is chiefly used for the under coats of varnish on a coach body.

This varnish is used for the surface coats of carriages, is pale in colour, and dries with a brilliant surface in about 12 hours. It is a very durable varnish, and will resist the destructive action of the atmosphere very well.

3. Elastic Carriage Varnish (1).—Run 8 lbs. of good quality gum copal, mix with $2\frac{1}{2}$ gallons of oil, add $\frac{1}{4}$ lb. of dried copperas and $\frac{1}{4}$ lb. of litharge, boil until it strings, then allow to cool and thin with $5\frac{1}{2}$ gallons of turps. Run 8 lbs. of second sort gum animi, mix with $2\frac{1}{2}$ gallons of oil, add $\frac{1}{4}$ lb. of dried sugar of lead and $\frac{1}{4}$ lb. of litharge, boil until it strings, allow to cool and thin with $5\frac{1}{2}$ gallons of turps. The two lots are mixed together, strained, and allowed to mature. This varnish dries hard with a fine polish in about 5 hours in summer and in about 7 hours in winter. It is used for varnishing common carriages and also for cabinet work.

4. Elastic Carriage Varnish (2).—Run 8 lbs. of first quality gum copal, mix with 3 gallons of oil, boil for 4 hours until it strings, then, after cooling, add $5\frac{1}{2}$ gallons of turps. Run 8 lbs. of best gum animi, mix with 2 gallons of oil, and, after boiling until it strings, thin with $3\frac{1}{2}$ gallons of turps. Two pots of this running are mixed with one pot of the first running, and the whole is strained and allowed to mature. This varnish is much used as the finishing varnish for common coaches, and for the under parts of superior coaches. It dries brilliant and is durable. It is rather quicker in drying than No. 1, taking about 10 hours in summer and 12 hours in winter.

5. Elastic Carriage Varnish (3).—Run 8 lbs. of gum copal, mix with 2 gallons of oil, and boil until it strings, then thin with $3\frac{1}{2}$ gallons of turps. Run 8 lbs. of gum animi, mix with 2 gallons

of oil, boil as before, and thin with $3\frac{1}{2}$ gallons of turps. Mix one pot of this running with one pot of the previous running, strain, and finish in the usual way. As good a quality of gums is not used in making this varnish as the last, so that it is usually rather darker, although it is quite as durable. It dries in about the same time.

6. Elastic Hard Carriage Varnish.—Run 8 lbs. of gum copal, mix with 2 gallons of oil, add $\frac{1}{4}$ lb. of dried sugar of lead, and boil until stringy; thin with $3\frac{1}{2}$ gallons of turps. Run 8 lbs. of gum animi, mix with 2 gallons of oil, add $\frac{1}{4}$ lb. of dried copperas, and boil until it strings; thin with $3\frac{1}{2}$ gallons of turps. Both runnings are mixed together and finished in the usual way. This varnish is used for the under coats in varnishing carriages; it dries hard in about 5 to 6 hours, and gives a smooth surface.

7. Carriage Varnish.—Run 8 lbs. of second quality gum animi, mix with $2\frac{3}{4}$ gallons of oil, add $\frac{1}{4}$ lb. each of litharge, dried copperas, and dried sugar of lead, boil until it strings, then thin with $5\frac{1}{2}$ gallons of turps, and finish in the usual way. This varnish is used for varnishing dark-coloured carriages, the iron-work of coaches, and for ordinary cabinet work. It dries quickly in about 4 hours in summer and 5 hours in winter, with a hard and glossy surface. It is not so durable as the other varnishes described above.

8. Pale Oak Varnish.—8 lbs. of gum copal are run and mixed with 3 gallons of oil; $\frac{1}{4}$ lb. each of dried copperas, dried sugar of lead, and litharge are added; the mixture well boiled and thinned with $5\frac{1}{2}$ gallons of turps, and the varnish strained and finished in the usual way. This varnish is used for all kinds of best cabinet varnish; it dries in about 4 hours with a hard and durable surface.

9. No. 2 Oak Varnish.—Made in the same way as the last, but from a poorer quality of gums.

10. Hard Church Oak Varnish.—Run 8 lbs. of gum kauri; mix with 3 gallons of oil; boil until it strings well; then, after cooling, thin with $5\frac{1}{2}$ gallons of turps. This varnish dries with a hard, glossy surface in from 6 to 7 hours. It is not a durable varnish if used in positions where it is exposed to the weather, but for all interior work it stands well and resists a great deal of wear and tear.

11. No. 2 Hard Church Oak Varnish.—This is made in the same way as the last, only poorer qualities of gums are used.

12. Pale Copal Varnish.—Carefully select 8 lbs. of the palest gum copal; run well and mix with 2 gallons of pale boiled oil; boil the whole until it strings, then allow to cool down a little,

and thin with $5\frac{1}{2}$ gallons of turps. Strain and finish as usual. When well made this varnish is very pale, and dries with a lustrous, durable coat in from 8 to 10 hours.

13. Japanners' Gold Size.—Run 10 lbs. of gum animi and mix it with 2 gallons of hot oil; prepare two runs of this. In the set pot place 10 gallons of oil and boil it well for 2 hours; then add 7 lbs. of red lead, 7 lbs. of litharge, and 3 lbs. of copperas; the addition of these driers is best made in small quantities at a time, the whole mass being kept boiling all the time; when all the driers have been added the boiling should be continued for about 3 hours longer. Sometimes the addition of the driers causes the boiling oil to froth up very much; in such cases it is best to reduce the fire somewhat, and to take some of the oil out of the pot, adding it again as the frothing subsides. When the oil has been boiled for 3 hours the two runs of gum are added, and the boiling is continued for 5 hours, when it will begin to string; the boiling is continued until the mass drops off the ladle or stirring rod in large drops, and strings well. Then allow to cool, which will take about 2 hours; pour in, in small quantities at a time, 30 gallons of turps; as this is being poured in the whole mass must be thoroughly stirred up so as to get the turps and varnish well mixed; the mixing with the turps must not be done too quickly, or otherwise there is too great a liability to boil over; in fact, this applies to the mixing of turps in making all these oil varnishes. This gold size will dry in about 10 minutes, if well made; although sometimes it may take 25 minutes to dry.

14. Black Japan (1).—This is made in a very similar manner to the gold size just described. Into the set pot put 6 gallons of linseed oil, boil it on a slow fire for 2 hours, then run in a gum pot 10 lbs. of asphaltum, and mix with 2 gallons of oil: when mixed, pour into the set pot; then run three more lots, pouring each one as it is run into the set pot; then add 7 lbs. of red lead, 7 lbs. of litharge, and 3 lbs. of copperas, in small quantities at a time; keep the mixture boiling slowly for 4 hours longer; then allow to stand till the next day, when it is boiled until a small quantity taken out on a glass will, when rubbed or rolled in the fingers, set hard; it is now allowed to cool, and when sufficiently cold 30 gallons of turps are added. If after the Japan has become cold it is found to be too stiff, then it can be warmed up and more turps added until it attains the right consistency. This Japan is used for all kinds of ironwork about carriages which are to be black; it dries with a hard, durable, lustrous coat in about 8 hours.

15. Black Japan (2).—A better quality of black Japan which

will dry harder and more glossy is made as follows:—Melt 48 lbs. of asphaltum in the set pot, and when melted add 10 gallons of oil; run in the gum pot 8 lbs. of common gum animi, and mix with it 2 gallons of oil; pour the mixture into the set pot; then run 10 lbs. of common amber, and mix with 2 gallons of oil; this running is also added to the set pot, the contents of which is boiled for 3 hours longer, during which time 7 lbs. of red lead, 7 lbs. of litharge, and 3 lbs. of copperas, are added, and the boiling continued until the mass sets between the fingers into a hard mass. Allow it to cool; then thin with 30 gallons of turps, as before.

16. Black Varnish for Carriage Iron Work.—Run 48 lbs. of asphaltum in the set pot, and add 10 gallons of boiled oil, 7 lbs. of red lead, 7 lbs. of litharge, and 3 lbs. of copperas; run 8 lbs. of copal, mix with 2 gallons of oil, and add to the set pot; boil the whole for 4 hours; place on one side till the next day, and then boil until it sets hard between the fingers; then, after cooling, thin with 30 gallons of turps. This dries hard with a good surface in about 3 hours.

17. Brunswick Black (1).—This very useful black varnish is made in several ways. Run 45 lbs. of asphaltum for 6 hours in a set pot. Boil 6 gallons of oil with 6 lbs. of litharge until it strings well; pour into the set pot with the asphaltum, and boil the whole until it will set hard between the fingers; then allow to cool, and thin with 25 gallons of turps. This dries in about 4 hours with a good surface, having a brilliant gloss.

18. Brunswick Black (2).—A commoner Brunswick black is made as follows:—28 lbs. of coal-tar pitch and 28 lbs. of asphaltum are boiled together in the set pot for 6 hours; the mixture is allowed to stand all night, after which it is boiled up and 8 gallons of boiled oil are added; 10 lbs. of litharge and 10 lbs. of red lead are added in small quantities at a time, and the mass boiled until it will set hard between the fingers; it is then allowed to cool, and is mixed with 20 gallons of turps. This will dry in about 1 to 2 hours, and is a good black varnish for all kinds of ironwork.

19. Black Leather Varnish.—A very good black varnish is made by boiling 10 lbs. of linseed oil with 4 lbs. of litharge for about 5 hours, and then colouring with lamp-black. Other leather varnishes will be found described under spirit varnishes.

20. Amber Varnish.—Run 6 lbs. of the palest amber, mix with 2 gallons of oil, and boil until it strings; then thin with $3\frac{1}{2}$ gallons of turps. This forms one of the most durable varnishes known; it is much used for varnishing pictures.

21. Copal Picture Varnish.—Run 8 lbs. of the very best

and palest copal, mix with 3 gallons of oil, and boil until it strings well; then thin with 3 gallons of turps. When good materials are used a pale durable varnish is obtained.

22. Oil Varnish.—Boil 6 gallons of linseed oil with 1 lb. of sugar of lead for 5 hours. Other driers may be used instead of the sugar of lead, such as sulphate of zinc, borate of lead, and borate of manganese. Only a very small quantity of the last is required, or about 1 lb. to 70 or 80 gallons of oil.

23. Gold Size.—Run 8 lbs. of gum copal, mix with 2 gallons of oil, boil until it begins to string, then add 6 gallons of boiling oil, and thin with turps to the required consistency. This does not dry as quickly as japanners' gold size, and, as its name indicates, is used for fastening gold leaf to glass and other objects.

GENERAL CONSIDERATIONS.—The following general features concerning oil varnishes and their manufacture should be noted. An oil varnish should possess the following properties:—1st, good and free working; 2nd, drying hard and rubbing freely; 3rd, giving an elastic coating not liable to crack or bloom, and which is resistant to the destructive action of the atmosphere. It is difficult always to secure these features of a good varnish, especially to combine the second and third, as hardness and elasticity are somewhat opposed to one another.

In the preparation of these varnishes too much care cannot be exercised in carrying out the various operations. The materials should be carefully selected; good varnish cannot be made from a poor quality of gum, and, no matter how good this may be, the use of a bad sample of oil will spoil any varnish made from it; the quality of the turpentine used also has some influence. In the sections referring to these materials will be found information as to the qualities required in good materials. The better the gum or resin is run, the larger will be the quantity of varnish obtained, and this will be stronger and better for working. The boiling of the oil and resin together must be well done; if not sufficiently boiled, the resulting varnish does not work freely, and is sometimes liable to bloom. This latter defect also occurs in varnishes made from badly-run gums. The stringing or boiling should be done slowly, and at as low a heat as possible; if brought forward too quickly by the use of too much heat, then the resulting varnish is liable to be discoloured. It takes more turps to thin it down, and the varnish neither works so freely under the brush, nor gives such a smooth brilliant surface as a good oil varnish should do. The more oil there is used in the composition of a varnish, the more elastic and less liable to crack

is the coat formed by the varnish. On the other hand, the drying is retarded by using too little oil. The more gum there is put into a varnish, the thicker, firmer, more quickly drying, and more brilliant when dry, is the coat formed; on the other hand, it is more liable to crack if there is too little gum. The varnishes made by the French method (which contain little oil) are rather liable to these defects of cracking, because of the want of elasticity in the coat they form.

Driers, especially copperas, when added to varnishes have a tendency to make the varnishes opaque, and to harden them. An oil varnish made with quick driers forms a coat which is hard, non-elastic, liable to crack, and of short duration.

The usual proportions of resins are for body varnishes about $1\frac{1}{4}$ to $1\frac{1}{2}$ lbs. per gallon; for carriage and cabinet varnishes, from 1 to $1\frac{1}{4}$ lbs. per gallon; for gold size and japans, from $\frac{1}{2}$ to $\frac{3}{4}$ lb. per gallon. If, after making and cooling, the varnishes are found to be too thick, they can be reduced to the required consistency by warming (so as to render them more fluid) and adding turps.

Varnishes should be kept at least six months after making before they are used; this ageing causes a better amalgamation of the constituents of the varnish, increases the ease with which it works under the brush, and causes it to form a smoother and more lustrous coat.

3rd. SPIRIT VARNISHES.

This class of varnishes consists chiefly of various resins dissolved in a volatile spirit, such as methylated spirit, turpentine, &c. Most of them are made without any oil, but some contain a small quantity of oil, which makes them more elastic and durable.

METHODS OF MAKING SPIRIT VARNISHES.

There are two methods of making this class of varnishes, depending on their containing or not containing oil, and on the nature of the resin or gum used in their preparation. The first method is very largely used in France, especially for making the oil containing varnishes; while the second is usually adopted in this country.

French Process of making Spirit Varnishes.—In the main this follows the plan already described for making oil varnishes, and the same plant can be used. The peculiarity of the varnishes made by this process is that they contain a

small quantity of oil; they might, therefore, be classed as oil varnishes, but, as the oil is merely of secondary importance, it has been thought best to class them among the spirit varnishes. These varnishes are made by running the gums as described under oil varnishes (p. 431); they are then mixed with the oil, which has been previously heated to the boil, and the mixture boiled until it strings, an operation only taking a few minutes to do; they are then allowed to cool, when they are mixed with the spirit, and finished in the usual way.

1. Amber Varnish.—Run 3 lbs. of pale amber, 3 lbs. of pale copal, and 3 lbs. sandarac together; boil 18 lbs. of linseed oil and, while very hot, mix with the melted resins; boil until stringy; then thin with sufficient turps.

2. Carriage Varnish.—Run 8 lbs. of sandarac, mix with 4 lbs. of boiled oil, boil till the mixture strings, and thin with 12 lbs. of turps.

3. Pale Copal Varnish.—Run 8 lbs. of the palest Sierra Leone copal, mix with 4 lbs. of boiled linseed oil, boil till stringy, and thin with 14 lbs. of turps.

4. Kauri Varnish.—Run 8 lbs. of pale kauri gum, mix with 4 lbs. of boiled oil, boil till it strings, and thin with 12 lbs. of turps.

Common Process of making Spirit Varnishes.—This method, which is the one commonly used in this country, is very simple. The resins are mixed with the solvent and kept in a warm place or gently heated until the resins are completely dissolved. It is, therefore, obvious that only those resins which are soluble in spirits (either naturally soluble or after fusion) can be used.

If it be found necessary to aid the solution of the resins in the spirits by the application of heat, the heating must be very gentle; as, owing to the volatility and inflammable vapours of the solvents used, too great a heat would cause a loss of the solvent and incur the risk of fire, which risk should be most carefully avoided.

For making these varnishes on a small scale, say about a gallon at a time, there is no better plan than that of using a large bottle which can be closed with a cork, and into this putting the materials and shaking them up from time to time. On the large scale no special plant is used, as a rule, as they are made in casks or any vessel ready to hand. A good form of plant for making the common spirit varnishes on a large scale would be a boiler-shaped vessel placed vertically; the lower half is fitted with a jacket of rather large dimensions to contain water, which can be heated by

steam if required; through the top end passes the vertical shaft of an agitator, and a manhole at the upper end serves as a feed-hole for the resins and spirits. In this apparatus the materials can readily be heated up to from 150° to 160° F. without danger, and this heat, together with the thorough mixing of the materials with the agitator, quickens the preparation of the varnish.

The methylated spirit used for making varnishes cannot be too strong, and should never be weaker than what is known as 65° over proof (see p. 382), as weaker spirits do not dissolve the various gums readily enough, especially such as mastic, sandarac, and Manila copal. Moreover, varnishes made with weak spirits are liable to dry somewhat dull, owing to the water in these spirits. As spirit is very liable to absorb water from the atmosphere it should be stored under conditions which will not allow of the access of moisture.

1. **French Polish.**—Shellac, 2 lbs.; gum benzoin, 4 oz.; spirit, 1 gallon. Mix together and shake, at intervals, until all the former two substances have dissolved.

2. **Shellac Varnish** is made by dissolving 1½ lbs. of shellac in 1 gallon of methylated spirit. This varnish is one of the commonest varnishes made; it dries in about 10 minutes, and yields a firm, hard, and lustrous coat, which is durable and resists the weather very well; by adding a little gum elemi or gum thus a varnish giving a more elastic coat is made. This varnish has a turbid appearance, and an orange-brown colour, and dries with a pale brownish colour. This varnish forms the basis of a large number of the coloured varnishes sold under the names of walnut varnish, mahogany varnish, &c., and made by colouring the shellac varnish with various colouring matters. The aniline dyes are found to be the best, as being the most soluble in the spirit, and, therefore, yielding the most transparent varnishes; these are sometimes sold as stains, although many of the stains which are sold are aqueous solutions of various colouring matters. These will be noticed later on.

3. **Mahogany Varnish.**—Shellac, 1½ lbs.; methylated spirit, 1 gallon; dragon's blood, 1 oz. This varnish is a poor imitation of the colour of mahogany. The following is a better one:—Shellac, 1½ lbs.; spirit, 1 gallon; Bismarck brown R, ½ oz.; nigrosine, a sufficient, but very small, quantity. Another kind of mahogany varnish consists of spirits 1 gallon, 1 lb. of gum sandarac, ½ lb. of shellac, 2 ozs. of Venice turpentine, and 4 oz. of dragon's blood.

4. **Walnut Varnish.**—Shellac, 1½ lbs.; spirit, 1 gallon; Bismarck brown R, 1 oz.; nigrosine, ½ oz. By varying the propor-

tion of the two colouring matters, the shade may be varied to a great extent.

5. Ebony Varnish.—Shellac, $1\frac{1}{2}$ lbs.; spirit, 1 gallon; brilliant spirit black, 2 ozs.

6. Brown Hard Spirit Varnish.—The following are a few recipes for making spirit varnishes which dry with a hard, firm, and lustrous coat:—(a) Sandarac, 1 lb.; shellac, $\frac{1}{2}$ lb.; gum elemi, 4 ozs.; Venice turpentine, 4 ozs.; spirit, 1 gallon. (b) Gum sandarac, 3 lbs.; shellac, 2 lbs.; spirit, 2 gallons; after the gums have dissolved add rosin turpentine varnish, 1 quart. This gives a good varnish, which is not as quick a drier as a pure spirit varnish. (c) A common brown varnish may be made by mixing shellac, $1\frac{1}{2}$ lbs.; rosin, $1\frac{1}{2}$ lbs.; spirit, 2 gallons.

7. White Hard Spirit Varnish.—This varnish is largely made for varnishing all kinds of cabinet work. Like the preceding, there are several ways in which it can be made. (a) Gum sandarac, $2\frac{1}{2}$ lbs.; gum thus, 1 lb.; spirit, 1 gallon. (b) Mastic, $\frac{1}{2}$ lb.; sandarac, 2 lbs.; elemi, 4 ozs.; spirit, 1 gallon. (c) Mastic, $\frac{1}{2}$ lb.; sandarac, 1 lb.; turpentine, 2 ozs.; spirit, 1 gallon. These dry quickly with a hard, lustrous coating. In use care is required not to work too rapidly, and to brush in one direction only, because if they are allowed to froth, as they are liable to do, they will have a dull surface when dry.

8. Mastic Varnish.—Gum mastic, 10 ozs.; and turpentine, 1 pint. Place the vessel in which the varnish is being made in a water bath, and keep at a gentle heat until the gum has dissolved. This varnish is much used for varnishing pictures. Genuine mastic varnish mixed with boiled oil forms a gelatinous mass known as “megilp,” which, owing to the ease with which it will work in oil painting, is often used as a vehicle by artists in oils; but it possesses several serious faults which make its use for painting pictures very undesirable. Raw linseed oil mixed with mastic varnish and a little acetate of lead forms a body known as “gumption,” which is also used as a vehicle in oil painting, but, as in the case of megilp, its use cannot be recommended.

9. Common Oak Varnish.—Common rosin, $3\frac{1}{2}$ lbs.; and turpentine, 1 gallon, are heated in a water-bath until the rosin has dissolved, when it is ready for use. This varnish dries in a short time with a hard, lustrous coat, which is not very durable, especially to rubbing.

10. White Shellac Varnish.—Bleached shellac, $1\frac{1}{2}$ lbs.; spirit, 1 gallon. The shellac must be thoroughly dried before it is added to the varnish; if used wet as it is sold the varnish made from

it will be dull and cloudy. Another method of making white shellac varnish is to dissolve $1\frac{1}{2}$ lbs. of shellac in 1 gallon of spirit, add about 2 lbs. of animal charcoal, and warm in a water-bath for 10 minutes; a little is now filtered; if the varnish is not sufficiently colourless more charcoal is added, and the warming continued. This process is repeated until the varnish is white enough; then it is filtered.

11. Paper Varnish.—(a) Gum sandarac, 20 ozs.; gum mastic, 8 ozs.; pale gum elemi, 2 ozs.; spirit, 48 ozs. This varnish dries quickly and forms a durable coat; the paper must have a coating of glue size before it is varnished. (b) Gum sandarac, 4 ozs.; gum mastic, 8 ozs.; gum thus, 6 ozs.; turps, 8 ozs.; spirit, 1 gallon. (c) Gum sandarac, 8 ozs.; Manila copal, 8 ozs.; copaiba balsam, 4 ozs.; castor oil, 2 ozs.; spirit, $\frac{1}{2}$ gallon.

12. Negative Varnish for Photographers.—Gum sandarac, 5 ozs.; gum benzoin, 2 ozs.; spirit, $\frac{1}{2}$ gallon.

13. White Varnishes.—(a) Pale Manila copal, 8 ozs.; camphor, 1 oz.; mastic, 2 ozs.; Venice turpentine, 1 oz.; spirit, 1 quart. This varnish dries quickly with a good surface. (b) Sandarac, 8 ozs.; mastic, 2 ozs.; Canada balsam, 4 ozs.; spirit, 1 quart. (c) Sandarac, 4 ozs.; dammar, 4 ozs.; gum thus, 8 ozs.; Manila copal, 8 ozs.; elemi, 8 ozs.; spirit, $\frac{1}{2}$ gallon. This is a good, pale and cheap varnish. (d) Gum thus, 8 ozs.; gum benzoin, 4 ozs.; Manila elemi, 4 ozs.; sandarac, 4 ozs.; spirit, $\frac{1}{2}$ gallon.

14. Dammar Varnish.—Gum dammar, 10 ozs.; sandarac, 5 ozs.; mastic, 1 oz.; turps, 1 pint. Digest at a gentle heat until the gums have dissolved.

15. Kauri Varnish.—Pale kauri, 8 ozs.; mastic, 4 ozs.; chloroform, 9 ozs.; spirit, 27 ozs. The spirit and the chloroform are mixed and then the resins are added.

16. White Spirit Varnish.—Pale Manila copal, 6 ozs.; dammar, 2 ozs.; bleached shellac, 2 ozs.; toluol, 6 ozs.; spirit, 18 ozs.

Coloured Varnishes.—These are mostly used for colouring metal work, when they are known as lacquers. For the colouring, such bodies as gamboge, accroides, dragon's blood, turmeric, &c., are used; while the coal-tar colours can be used to make a great variety of coloured varnishes, red, blue, green, brown, yellow and other more or less fancy colours.

17. Lacquers.—Generally these are weak shellac varnishes coloured with various colouring matters. The introduction of the coal-tar colours has enabled a great many fancy-coloured lacquers to be introduced of recent years. Lacquers are used almost exclusively for colouring metals. They are used in two

ways called "cold lacquering" and "hot lacquering." In the former method the lacquer is applied with a brush as evenly as possible over the article while it is cold; then this is put into an oven, where it is subjected to a gentle heat for about two minutes to set and harden the lacquer; care has to be taken that the oven is not too hot. In the second method the articles are first slightly heated, about as hot as can be borne by the hand; then the lacquer is brushed over them. If the article is small it is put into a hot oven for a minute; if large, there is hardly any necessity for this, as it will keep its heat long enough to set the lacquer.

(a) *Pale gold lacquer*.—10 ozs. of orange shellac, 1 gallon of spirit, and $\frac{1}{2}$ oz. of gamboge. (b) *Deep gold lacquer*.—Orange shellac, 10 ozs.; turmeric, 4 ozs.; gamboge, 4 ozs.; dragon's blood, $\frac{1}{2}$ oz.; spirit, $\frac{3}{4}$ gallon. (c) *Pale lacquer*.—1 gallon of spirit, 5 ozs. of orange shellac, 4 ozs. of gum sandarac, 1 oz. of gum elemi and 1 oz. of gamboge. (d) *Brass lacquer*.—14 ozs. of shellac, 4 ozs. of turmeric, 1 oz. of annatto, $\frac{1}{2}$ oz. of saffron, and 1 gallon of spirit. (e) *Deep lacquer*.—10 ozs. of shellac, 6 oz. of sandarac, 2 ozs. of gum elemi, 2 ozs. of dragon's blood, and 1 gallon of spirit. (f) *Gold lacquer*.—10 ozs. of shellac, 1 gallon of spirit, and $\frac{1}{4}$ oz. of aniline yellow. (g) *Green lacquer*.—10 ozs. of shellac, 1 gallon of spirit, and $\frac{1}{4}$ oz. of brilliant green. This gives a blue green shade. (h) *Green lacquer*.—10 ozs. of shellac, 1 gallon of spirit, $\frac{1}{8}$ oz. of methyl green, and $\frac{1}{8}$ oz. of auramine; this will give a yellowish-green. (i) *Bronze green lacquer*.—10 ozs. of shellac, 1 gallon of spirit, $\frac{1}{8}$ oz. of brilliant green, and $\frac{1}{8}$ oz. of chrysoidine. (j) *Blue lacquer*.—5 ozs. of shellac, 5 ozs. of sandarac, 2 ozs. of elemi, 1 gallon of spirit, and 1 oz. of alkali blue. (k) *Violet lacquer*.—8 ozs. of sandarac, 2 ozs. of shellac, 3 ozs. of elemi, 1 gallon of spirit, and $\frac{1}{4}$ oz. of methyl violet. These examples will serve to show how the coal-tar colours can be used in the preparation of lacquers. A great variety can be thus made by changing the colouring matter used. With some of the so-called aniline colours care should be taken not to use too much, as then the real colour of the dyestuff is not developed but a bronzy green appearance only; this is likely to happen with magenta, the violets and greens. It may also be mentioned that the blues, violets, and some other colours are made in several shades distinguished by letters, as 3R, 2B, 5B, 6G, &c.; in such cases care must be taken as to the particular brand of colour used, for example, there is a great difference in shade between violet 3R—a very red shade—and violet 6B—a very blue shade.

18. Varnish Paints.—These can be made by simply adding colour to any of the varnishes described above. It will, there-

fore, scarcely be necessary to give recipes in detail for the preparation of these; a few notes about them and the colours to be used will suffice. This class of varnishes may be classed into two divisions—1st, those which dry with a more or less opaque surface similar to a paint but with the lustre of a varnish; 2nd, those which dry with a transparent lustrous surface. The former, perhaps, may be called varnish paints; the latter, varnish stains. Varnish paints owe their colour to opaque pigments, such as vermilion, Prussian blue, emerald green, chrome yellow, &c. There is no difficulty in making these; simply adding a required colour or pigment in sufficient quantity to any varnish is all that is necessary. It will be found advisable to use those pigments which are the lightest in weight; heavy pigments like vermilion, red lead, barytes have too much tendency to settle out from the varnish to work satisfactory. Some cheap varnish paints are made from rosin spirit, rosin and pigment. Varnish stains owe their colour to colouring matters which are soluble in the varnish. A great variety of soluble colours, of both natural and artificial origin, can be used for this purpose. As with the varnish paints any required colour of stain can be obtained by simply adding the necessary colouring matter, which, in this case, must, however, be soluble in the spirit, so that a transparent coloured liquor is obtained. Any of the coal-tar colours soluble in spirit may be used; these have been described above (p. 424); turmeric, annatto, accroides, and other natural colours can also be used.

19. Crystal Varnish.—1 lb. of Canada balsam is dissolved in 1 pint of turps.

20. Gold Varnish.—Shellac, 8 ozs.; sandarac, 8 ozs.; mastic, 8 ozs.; gamboge, 2 ozs.; dragon's blood, 1 oz.; turmeric, 4 ozs.; and spirit, 1 gallon.

21. Black Leather Varnish.—Shellac, 12 ozs.; gum thus, 5 ozs.; sandarac, 2 ozs.; lamp-black, 1 oz.; turpentine, 4 ozs.; and spirit, $\frac{3}{4}$ gallon.

22. Common Red Varnish.—Rosin, $2\frac{1}{2}$ lbs.; coal-tar naphtha, 1 gallon; and red oxide of iron sufficient to give the required colour. By substituting other colours for the red, various coloured varnishes may be made.

23. Furniture Varnish.—Shellac, $1\frac{1}{2}$ lbs.; sandarac, 4 ozs.; mastic, 4 ozs.; and spirit, 1 gallon.

24. Dammar Varnish.—Dammar, 10 ozs.; sandarac, 5 ozs.; mastic, 1 oz.; and turps, 20 ozs. Digest at a gentle heat until dissolved; if necessary add more turps to bring down to the proper consistency.

25. Black Varnish.—Asphaltum, 1 lb.; wax, 1 oz.; lamp-black, $\frac{3}{4}$ oz.; and turps, 2 pints.

26. Common Black Varnish.—Coal-tar pitch, 1 lb.; coal-tar, 2 ozs.; boiled oil, 2 ozs.; and coal-tar naphtha, 1 gallon. If not black enough, add sufficient lamp-black to bring the colour up.

27. Picture Varnish.—Sandarac, 2 ozs.; mastic, 4 ozs.; capivi balsam, 1 oz.; gum thus, 3 ozs.; turps, 4 ozs.; and spirit, 3 pints.

4th. WATER VARNISHES.

This group comprises but few and little used varnishes.

1. Lac Water Varnish.—Shellac, 6 ozs.; borax, $1\frac{1}{2}$ ozs.; and water, 1 pint. Boil together until the lac is dissolved. If bleached lac is used a white varnish will be made; if the orange shellac, the varnish will have a pale brown colour. This varnish makes a fair vehicle for water colours; it is a good paper varnish, and dries with a fair lustre and with a hard coat which is waterproof. By adding any of the soluble coal-tar colours coloured varnishes can be made.

2. Glazing Varnish.—Mix 1 pint of white of egg with 1 pint of water. A little carbolic acid or salicylic acid or, better, thymol should be added to preserve this varnish. This varnish or glaze dries with a fair amount of lustre. If, after being applied, it be placed in a hot room to dry, the coat will be made more waterproof. Dried albumen may be used instead of the white of egg by dissolving 1 oz. in 1 pint of water; only the colour of the glaze is not so good.

3. Glue varnish is made by dissolving 1 lb. of good pale glue in 2 gallons of water. The colour of this varnish depends very much on the quality of the glue used; if the best gelatine, then a white varnish will be made; if a brown glue, then a brown varnish. This varnish is not very good because of the sticky coat it gives which is not waterproof; by adding just before using, a small quantity of bichromate of potassium (1 oz. in 2 gallons), the coat becomes nearly waterproof. It is important that the bichromate be added only just before use, as it would act on the varnish and cause it to set into a gelatinous unworkable mass. This varnish forms the basis of some leather varnishes. A little thymol or borax may be added as a preservative.

4. Crystal Water Varnish.—1 lb. of good white gum arabic and 1 lb. of glucose are dissolved in 3 pints of water. This dries hard, with a gloss.

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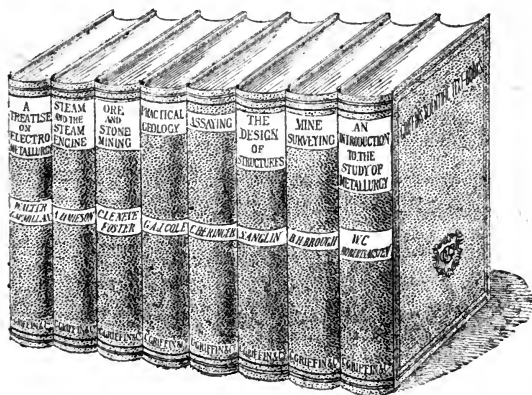
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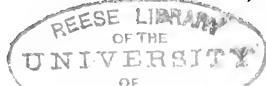
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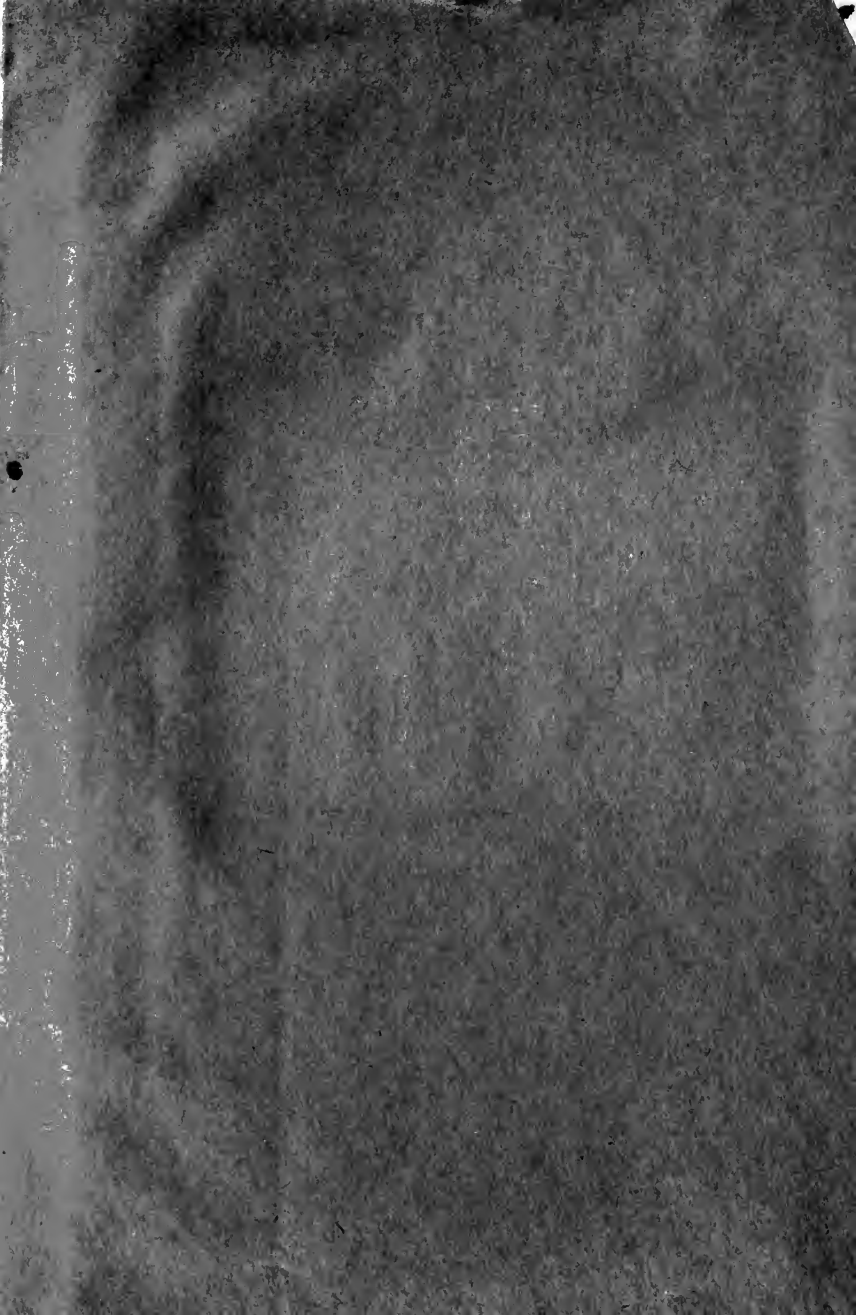
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