THE MANUFACTURE OF LAKE PIGMENTS
FROM ARTIFICIAL COLOURS
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PREFACE.

In revising the matter for this edition, it was considered that it would be more in sequence if the section dealing with the sketch of the organic compounds at the beginning of the book in the previous edition were transferred to the last chapter.

There has been no deviation from the object of dealing with the chemical and physical problems which arise in the production of lake pigments in such a manner as to aid the lake-maker to devise his own methods and formulae, and avoiding, in so far as possible, definite recipes which may be good under one set of conditions but of no use in others.

The production of lake pigments at the present time is very difficult, for, with the disappearance of the German dyestuffs from the market, there is great difficulty in obtaining reliable dyes that will produce constant results; for this reason the German names of dyestuffs have been retained in many instances, in order that those who are fortunate enough to have samples of these dyestuffs can readily compare them with what is now offered.

Lake-making demands the best possible dyestuffs, for in most cases a lake when once formed cannot
be altered, and irregular shades in various deliveries are ruinous to the reputation of the firm making them. The pigment trade is one of the largest users of dyestuffs; it is to be strongly urged that the British dyestuff manufacturer will devote very serious attention to this important industry and regard it as equally important as the dyeing trade.

I am deeply indebted to W. Davison, B.Sc., A.I.C., and W. E. Merry, Esq., both of the Directorate of Chemical Inspection, Royal Arsenal, Woolwich, for their valuable assistance in reading and correcting the proofs.

The British Dyestuffs Corporation (Huddersfield), Ltd., Huddersfield, have at great trouble and with much care been so good as to prepare the lakes and the plates for this edition, and I must make the most sincere acknowledgment and thanks for their help and kindness in this matter.

F. H. JENNISON.

Newcastle-on-Tyne,
December, 1919.
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THE
MANUFACTURE OF LAKE PIGMENTS
FROM ARTIFICIAL COLOURS.

CHAPTER I.
INTRODUCTION.
The generic term "lake colour" is applied to all pig-
ments made from dyestuffs and colouring-matters, by
precipitation of the colouring-matter as an insoluble
compound, and serves to distinguish such colours from
natural pigments, such as ochre, umber, etc., and from
chemical colours manufactured by direct combination or
decomposition of distinct salts, e.g., such colours as lead
chromates, Chinese blue, emerald green, etc.

Prior to the introduction of the coal-tar dyes, lakes were
made from the natural dyestuffs—cochineal, sapan wood,
logwood, Lima wood, fustic, flavin, weld, etc. Many of
these lakes are still in the market, and are known by such
names as crimson lake, berry yellow, madder lake, Dutch
pink, rose lake, leather lake, etc.; but of recent years, ex-
cept for some few and particular purposes, they have been
superseded by lakes made from artificial colours, because
the latter can be produced more easily and cheaply, and
possess greater staining power, brilliancy, and constancy
of shade.

The application of colouring-matters to lake manu-
facture is not without difficulty. Lakes intended for the
preparation of linoleum colours, lithographic and ink pigments, paint grinding, and surface and wall papers, each have their own particular requirements, and the nature and properties of each pigment must be such as to render it suitable for the particular purpose for which it is required. Dyestuffs cannot be produced if there be not a definite known demand for them, and the closest co-operation between lake makers and dye manufacturers is therefore essential, if success is to be assured.

In the past the British dye firms have catered almost exclusively for the colour requirements of the textile trades, paying little attention to those of the pigment manufacturers, who readily obtained their supplies from abroad at prices generally lower than those ruling for home products.

The closing of the continental source of dyestuffs greatly increased the difficulties of the lake manufacturer, for it was impossible for the British manufacturers to meet the increased demands of the textile trades and the new demand of the lake maker, since the particular requirements of the latter were practically unknown to them. Their difficulties have been further increased by the fact that the greater part of their plant was urgently required for the production of explosives.

It is, however, very important that the requirements of the lake trade be not overlooked. A little consideration will show that the consumpt of artificial dyes in the production of lake pigments is of very considerable magnitude, if not greater than that in any other industry.

The technology of lake pigment making differs materially from that of the dyeing trades. It is essential that the British and allied dyestuff manufacturers give very considerable attention to these requirements, and to the
peculiarities of the various branches of manufacture in which lake pigments form an important item. It is not unknown that the great German firms spared neither trouble nor expense to produce a particular colour to match not only the required shade but also particular properties required for some special purpose. They learned much of the technical difficulties and requirements, not only of the lake makers but of the users of the pigments also. By this means they laid the foundation of their industry, gathering knowledge and information enabling them to deal with future difficulties of the same nature. They became cognizant of the weaknesses of the materials in use, and worked toward replacing them by very much superior articles. An example of this striving for more suitable materials is readily seen in the substitution of lithol reds for dyes of the eosine class; the latter were largely used for royal reds and vermilionettes. They were certainly very brilliant, their fastness to light being deplorable. The introduction of the lithol reds very rapidly caused, save for some special purposes, the disappearance of this class of pigment from the market. The permanent and pigment reds have replaced the eosine vermilionettes; because of the great permanency of the pigments from the newer class the demand for them has grown very considerably.

The British dye firms, being hard pressed to meet the wants of the textile trades, and handicapped by necessary production of munitions, could not give much attention to this branch, but if some attention be not given in the near future, the lake manufacturers will be compelled to revert to those who, from accumulated knowledge of their requirements, are ready to supply their particular needs.
If the best and most economical results are to be secured in the manufacture of lakes from artificial dye-stuffs, and each lake is to be adapted correctly to the purpose for which it is required, some knowledge of the chemistry, constitution, and properties of the colours used is necessary.

With the difficult and intricate chemistry of the production of the artificial dyestuffs the lake manufacturer need not be familiar, but a knowledge of the chemical nature of the colour he is using is essential; e.g., the reason why he cannot precipitate magenta with barium chloride when a scarlet is easily thrown down by this reagent requires his careful attention. A study of the constitution of colouring-matters will show that the nucleus of the molecule of any given colour is not, from the actual lake-producing point of view, the essential feature of the colour, the substitution and addition products of the chromophor are of vastly greater importance. For instance—

Tropaolin OO is phenyl-amido-azo-benzene sulphonic acid—

\[
\text{HSO}_3\text{C}_6\text{H}_4\text{N} : \text{N} - \text{C}_6\text{H}_4\text{NHC}_6\text{H}_5
\]

or \( \text{C}_6\text{H}_4\{\text{SO}_3\text{H} \}	ext{N} : \text{N} \cdot \text{C}_6\text{H}_4\text{NHC}_6\text{H}_5 \)

The chromophor of this colour is azo-benzene—

\( \text{C}_6\text{H}_5\cdot\text{N} : \text{N} \cdot \text{C}_6\text{H}_5 \)

From examination of the formula given, it is seen that in one of the benzenes of the diazo-benzene, one of the hydrogens has been substituted by the sulphonic acid group, and in the other by an amido-benzene.

This being an acid colour, the latter substitution will be found to have no influence on the dyeing or lake-forming properties of the colour, but affects the colour of the dye by intensifying the shade, acting in this case only as
an auxochrome, as Witt names this property of certain organic radicles.

The lake-forming properties of Tropaolin OO depends only on the sulphonic-acid group present.

The artificial colouring-matters are divided into several classes, according to the molecular configuration of the nuclei.

The usual classification is—

I. Nitro colours.
II. Azo colours.
III. Nitroso and isonitroso colours.
IV. Oxyketone colours.
V. Ketonimides and hydrazides.
VI. Triphenylamine colours.
VII. Azines, oxazines, and thioazines.
VIII. Quinoline colours.
IX. Acridine colours.
X. Sulpho colours.

It is possible from a purely chemical aspect to increase this list very considerably, but, as the knowledge of the relations between the constitution and the chromatic properties of the various groups is by no means perfect, and as the minor differences in the grouping of the molecules or radicles in the nuclei are of but little importance in the production of lakes, it would be of little profit to enter into the question very minutely.

Before discussing the constitution of the colours in the various groups, an explanation of the terms used in describing the several parts of a colour molecule, and of the various organic compounds and combinations which frequently occur in or compose the various dyestuffs, will be advantageous:—
A chromophor group is the colour-giving group.
A chromogen, a molecule containing only a chromophor.
Salt-forming group, a group which imparts acid or basic properties to a colouring-matter.
An auxochrome group, one which, though it may impart acid or basic properties to the colouring-matter, intensifies and alters the shade of the colour.

An organic radicle is a group of atoms which go through a series of compounds without alteration, can be replaced in these compounds by a simple body, and, when combined with an element, such element may be substituted by some simple body. The methyl-radicle, CH₃, when combined with hydrogen forms methane, CH₄, which, when treated with iodine, gives iodo-methane, CH₄ + I₂ = CH₃I + HI. Acting on iodo-methane with sodium, we get ethane, 2CH₃I + Na₂ = 2NaI + 2CH₃, and this hydrocarbon, when treated with iodine, forms iodo-ethane, C₂H₅I. On the addition of ammonia, iodo-ethane forms ethylamine, C₂H₅I + NH₃ = C₂H₅NH₂ + HI; when ethylamine is combined with nitrous acid it forms ethylamine nitrite, which, when heated, yields alcohol, C₆H₅NH₂NO₂ = N₂ + H₂O + C₂H₅OH. Oxidation of alcohol gives acetic acid, CH₃COOH, the sodium salt of which, when treated with caustic soda, yields methane. Thus, CH₃COONa + NaOH = CH₄ + Na₂CO₃, showing that after many changes the radicle, CH₃, remains unaltered.

In organic chemistry the compounds are divided into two series, the fatty and the aromatic, or the derivatives of methane and benzene; it is from the latter that the dye-stuffs are derived, but the radicles of the methyl series take part as substituent groupings in many combinations of benzene nuclei. The nature of these combinations is
dealt with in Chapter XIV., and is arranged in such a manner as, it is hoped, will afford a guide to the study of those combinations yielding dyestuffs from which lakes are produced.

A survey of the whole problem of the manufacture of lake pigments from artificial colours resolves itself into three main divisions, which may be summed up as follows:

(a) The study of the composition, and chemical and physical properties of the dyestuffs or colouring-matters, suitable for the preparation of lakes.

(b) The chemistry of the reagents used, and the reactions and combinations which occur between these reagents and the colouring-matters in the production of lakes.

(c) The nature and function of the base substrata or matrix, and its action on the nature and application of the resultant pigment.

In the study of the chemistry of the dyestuffs, it will be seen that they are nearly all definite chemical compounds, some of a very complex character it is true, but still capable of fairly simple consideration from the point of view of their reactions; and, from whatever source they may be obtained, the synonyms of both British and foreign manufacture are reasonably constant in their chemical composition and properties, though the actual strength and peculiar physical characteristics may show slight differences. Attention and careful study must be given not only to the chromophoric group and auxochromic groups, but to those radicles in the dyestuff which give to it the distinctive chemical properties of the class to which it belongs.

The reagents used in the transformation of soluble dyestuffs into insoluble compounds, available for use as pigments, require careful study: they must be classified according to general properties, and the special character-
istics of the individual members of each group considered. In addition, when both basic and acid radicles occur in the molecule of a dyestuff, combination of two or more precipitating agents may be necessary, and they must be so chosen as to secure the maximum result.

Having decided the nature of the dye to be used, and the most suitable reagent or reagents for its precipitation, there still remains the question of the base on which the dye is to be precipitated. Almost invariably the suitability of a lake pigment for any particular application is governed by the nature of the base or matrix with which it is combined. Although lithol red precipitated on barytes would be satisfactory as a paint or linoleum pigment, it would be useless for lithographic work owing to the comparative coarseness of the matrix, and could be rendered suitable for the latter only by the substitution of blanc fixe—precipitated barytes—for the coarse barytes employed.

The function of the base is not one simply of loading or diluting a lake pigment. Apart from their physical condition being such as to render impossible the complete utilization of their tinctorial power, many of the lakes are useless in the pure state as pigments, owing to hardness and lack of body when dry. The base, therefore, must be regarded as an integral part of the lake pigment, and, as such, needs very careful discrimination in selection. The purpose for which the pigment is to be used must be in all cases the paramount guiding principle.

It is with the practical application of the three branches of lake manufacture from artificial colours that it is proposed to deal in the following chapters.
CHAPTER II.

THE CLASSIFICATION OF THE ARTIFICIAL COLOURING-MATTERS.

The Nitro Group.—The chromophor of this group is the nitro-radicle, NO₂, which, when combined with the amines and phenols of the aromatic series, produces dyestuffs of an acid character. The nitro-amido compounds, owing to the basic properties of the amido group, are of but little value, being of much less tinctorial power than those of the phenols. Only one sulphonic acid of this group of commercial value is in the market, namely, naphthol yellow S. The chief application of the colours of the nitro group in lake-making is to modify the shade of basic colours with which they combine, in some cases totally, but usually only partially precipitating them. The precipitation of the basic colours by other means usually carries down the whole of the colouring-matter. Certain members combine partially with aluminium hydrate, Al₂(OH)₆, but, on heating and washing, the products are almost completely redissolved. Of the colours in this group those most generally met with are—

Pieric acid, C₆H₂OH(NO₂)₂, naphthol yellow, and naphthol yellow S.

Naphthol yellow, dinitro-α-naphthol, C₁₀H₅OH(NO₂)₂,
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usually comes into commerce as the sodium salt, \( C_{10}H_5\text{ONa} (\text{NO}_2)_2 \). Naphthol yellow S, the sulphonic acid of naphthol yellow, \( C_{10}H_4(\text{OH})(\text{NO}_2)_2\text{SO}_3\text{H} \), the sodium salt of which, \( C_{10}H_4\text{ONa}(\text{NO}_2)_2\text{SO}_3\text{Na} \), is usually sold, combines with freshly precipitated aluminium-hydrate, partially forming a pale yellow lake. A more complete precipitation of the colour is secured, when the requisite quantity of barium chloride is used. In the presence of purely basic colours, naphthol yellow S is co-precipitated, but, after a time, separates out; and the most complete precipitation is secured only when it is used in conjunction with amido-sulphonic-azo colours, and precipitated on a base in which there is freshly precipitated aluminium hydrate, by means of barium chloride. In these cases it evidently combines with the basic group of the colour used and with the aluminium hydrate, the complex giving, on the addition of barium chloride, a compound lake. Green lakes prepared in this manner are much faster to light than those produced by using other yellow dyestuffs.

The Azo Group.—The azo dyestuffs are characterized by the fact that they contain the chromophor, \(-\text{N} = \text{N}-\), linked up to two benzene rings or other aromatic hydrocarbons. They form several well-defined groups, which may be classified as follows:

1. Amido-azo colours.
2. Oxy-azo colours.
3. Tetrazo dyestuffs.

There are some other groups of minor importance, individual members of which are used in the preparation of lakes, but these can readily be considered in conjunction with the other groups to which they are related.

Before proceeding to the detailed consideration of the azo colours,—by far the most numerous of artificial dye-
stuffs,—it will be as well to discuss briefly their general formation, and the influence exercised on their colouring powers and properties, by the introduction of various hydrocarbons and their substitution products into the colour molecule.

During recent years the azo-compounds have become of importance to the pigment maker, owing to the introduction of many dyes of this class into the market as pigment or permanent colours. The latter are simply azo colours of bright shades and great colouring power, which are frequently mixed with some substrata and sold as pigments. Some contain one sulphonic-acid group and are fixed or modified by the use of barium and calcium salts; others are insoluble azo-compounds which are really pigments in themselves, but are not of much use in the arts as such, although they lend themselves readily to the production of useful pigments. On account of their great strength the so-called pigment and permanent colours can impart their shade to a high proportion of base or substrata. The nature and application of this class of artificial colouring-matter is dealt with fully in Chapter X.

The highly coloured azo-compounds are not really dyestuffs unless they contain some body imparting acid or basic properties. For instance, azo-benzene, though a brilliantly coloured body, does not possess dyeing properties until it is sulphonated, i.e., converted into the sulphonic acid of azo-benzene, when it acquires tinctorial powers, which, however, are considerably increased by the introduction of an auxochrome group like (OH). The introduction of the amido-radicle confers basic properties on the compound; and, whereas the acid azo-compounds have to be sulphonated to render them soluble, the basic are usually so without further treatment. They combine
with acids, however, to form salts. The introduction of the various auxochrome groups exercises great influence on the colour produced, more especially if they be of an entirely different nature from those constituting the parent colour.

The compounds which contain only hydrocarbons of the benzene series are yellow, orange, and brown. The introduction of naphthalene changes the colour to red; and, as the number of naphthalene rings increases, they become bluer, yielding violets and various shades of blue.

*The Amido-azo Colours.*—The amido-azo colours are of a basic nature. Some members of this section come into commerce as sulphonic acids although the majority are simply the amido-derivatives. Though both the amido- and sulphonic-acid groups confer certain properties on the colour molecule, the one being basic and the other acid in nature, it is only when these two opposite characteristics are satisfied that the best results can be looked for.

To attempt to give a detailed list of the colours of this division alone would be of little value, since there are many such lists already in existence. As a general rule they can be regarded as members of the same family, answering to the same reactions in respect of precipitation and lake-forming. It is proposed to deal with the chief representatives only:

Chrysoidine : diamido-azo-benzene, $C_6H_4 \cdot N \cdot C_6H_2(NH_2)_2$  
Diphenylamine Orange or Acid Yellow D : sodium salt of p.-sulphobenzene-azo-diphenylamine,

$$C_6H_4\{\begin{array}{l}(4)SO_3Na \\ (1)N : N-(1)C_6H_4(4)NH \cdot C_6H_5\end{array}$$

A very good work of reference dealing with the constitution, formula, and properties of the artificial colours is Schultze and Julius' *The Systematic Survey of the Organic Colouring Matters* (last edition, 1914).
Metanil Yellow: the sodium salt of meta-sulphobenzene-azo-diphenylamine,

\[ C_6H_4\left\{(3)SO_3Na \atop (1)N : N(1)C_6H_4(4)NH \cdot C_6H_5 \right\} \]

Acid Brown R: salt of p.-sulphonaphthalene-azo-phenylene diamine-azo-benzene,

\[ C_{10}H_6\left\{(4)SO_3Na \atop (1)N : N \atop C_6H_5 \cdot N : N \atop C_6H_2 \right\} \left\{(1)NH_2 \atop (3)NH_2 \right\} \]

Bismarck Brown: hydrochloride of benzene disazo-phenylenediamine,

\[ C_6H_4\left\{(1)N : N \atop (2)NH_2HCl \atop (4)NH_2 \right\} \left\{(2)NH_2 \atop (2)NH_2 \cdot HCl \atop (4)NH_2 \right\} \]

When sulphonic-acid groups are absent from the colour molecule, the colouring-matter can be thrown down as a lake by those means usually adopted for purely basic colours, e.g., by combination with tartar emetic and tannic acid.

When the sulphonic-acid group is present, barium chloride precipitates the bulk of the colour in most cases, but the precipitation is usually not complete. The addition of a little oleic acid, previous to the addition of the barium chloride, renders the precipitation more complete, and greatly increases the fastness and brilliancy of the lake produced. This is very noticeable in the case of metanil yellow.

The Oxy-azo Colours.—The most important members of this group are the derivatives of the isomeric naphthols and their sulphonic acids. Of the colours derived from
benzene, the most important is Tropaolin O, or Resorcine Yellow: the sodium salt of p.-sulphobenzene-azo-resorcinol,

\[
\begin{align*}
C_6H_4 & \{ (4) \text{SO}_3 \text{Na} \\
(1) \text{N} : \text{N}(4)C_6H_3 & \{ (1) \text{OH} \\
(1) \text{N} : \text{N}(1)C_6H_3 & \{ (3) \text{OH}
\end{align*}
\]

The naphthol-azo dyes are almost entirely used in the form of, sulphonic acids. The sulpho group has very little influence on the shade, but the different isomeric naphthol-sulphonic acids give entirely different shades with the same diazotized base. The derivatives of \( \beta \)-naphthol are found to be more permanent than those of \( \alpha \)-naphthol, owing no doubt to the method of arrangement of the various substitution groups in the naphthalene ring.

When the naphthol-sulphonic acids are combined with the diazo-compounds of benzene, yellow and orange colours are produced; with the higher homologues the colours become red; and with the derivatives of naphthalene we have again reds, which become more blue with increasing molecular weight of the compounds. The colours known as the coccinines are derived from diazoanisol and its homologues and \( \beta \)-naphthol disulphonic acid.

The oxy-azo colours are very numerous, and vary in colour from yellow to deep bluish-red. Of those which demonstrate the constitution of this group the following examples are given:

Orange 2.—Sodium salt of p.-sulphobenzene-azo-\( \beta \)-naphthol,

\[
\begin{align*}
C_6H_4 & \{ (1) \text{SO}_3 \text{Na} \\
(1) \text{N} : \text{N}(1)C_{10}H_6 & \{ (2) \text{OH}
\end{align*}
\]

Mandarin G. R.—Sodium salt of sulpho-o.-toluene-azo-\( \beta \)-naphthol,

\[
\begin{align*}
\text{SO}_3 \text{Na} \cdot C_6H_3 & \{ (2) \text{CH}_3 \\
(1) \text{N} : \text{N}(1)C_{10}H_6 \cdot \text{OH} & \{ (2)
\end{align*}
\]
Ponceau 2 G.—Sodium salt of benzene-azo-β-naphthol disulphonic acid,

\[
C_6H_5\cdot N : N \cdot (1)C_{10}H_4 \left\{ \begin{array}{l}
(2)\text{OH} \\
(3)\text{SO}_3\text{Na} \\
(6)\text{SO}_3\text{Na}
\end{array} \right.
\]

Ponceau 3 R.—Sodium salt of ψ cumine-azo-β-naphthol disulphonic acid,

\[
C_9H_2 \left\{ \begin{array}{l}
(5)\text{CH}_3 \\
(4)\text{CH}_3 \\
(2)\text{CH}_3 \\
(1)\text{N} : N \cdot C_{10}H_4 \end{array} \right\} \left\{ \begin{array}{l}
\text{OH} \beta \\
(\text{SO}_3\text{Na})_2
\end{array} \right.
\]

Ponceau 2 R.—Sodium salt of xylene-azo-β-naphthol disulphonic acid,

\[
C_{10}H_4\text{(CH}_3\text{)}_2 \cdot N : N \cdot (1)C_{10}H_4 \left\{ \begin{array}{l}
(2)\text{OH} \\
(3)\text{SO}_3\text{Na} \\
(6)\text{SO}_3\text{Na}
\end{array} \right.
\]

Fast Red B, or Bordeaux B.—Sodium salt of α-naphthalene-azo-β-naphthol disulphonic acid,

\[
C_{10}H_7\text{(a)} \cdot N : N \cdot C_{10}H_4 \left\{ \begin{array}{l}
(2)\text{OH} \\
(3)\text{SO}_3\text{Na} \\
(6)\text{SO}_3\text{Na}
\end{array} \right.
\]

Croceine Scarlet B. X.—Sodium salt of sulphonaphthalene-azo-β-naphthol monosulphonic acid,

\[
C_{10}H_5 \left\{ \begin{array}{l}
(4)\text{SO}_3\text{Na}.
\end{array} \right\} \left\{ \begin{array}{l}
(1)\text{N} : N \cdot (2)C_{10}H_5 \end{array} \right\} \left\{ \begin{array}{l}
\text{OH} \beta \\
(\text{SO}_3\text{Na})_2
\end{array} \right.
\]

*The Tetrazo Dyestuffs.*—The tetrazo or disazo colouring-matters are of a much more complex nature, and differ from the azo colours in that they contain the chromogen 'N : N' more than once in the molecule. They may be divided into three classes:—

(a) Those which contain two azo groups and the auxochrome groups in one benzene nucleus, e.g., phenol-disazo-benzene,

\[
C_6H_5\cdot N : N \cdot C_6H_3 \left\{ \begin{array}{l}
\text{OH} \\
N : N \cdot C_6H_5
\end{array} \right.
\]
(b) Those which contain the disazo groups in one ring and the auxochromes in the others. Tetrazo-benzene-phenol,

\[ \text{C}_6\text{H}_5\text{N} : \text{N} \cdot \text{C}_6\text{H}_4\text{N} : \text{N} \cdot \text{C}_6\text{H}_4\text{OH}\]

(c) The disazo dyestuffs derived from benzidine,

\[ \begin{align*}
\text{C}_6\text{H}_4\text{NH}_2 \\
\text{C}_6\text{H}_4\text{NH}_2
\end{align*} \] 

and its homologues.

Without entering into minute details concerning the formation and the chemical peculiarities of each of these groups, their general formation may be represented by the following few examples of this extremely numerous class:

Biebrich Scarlet.—Sodium salt of sulphobenzene-azo-sulphobenzene-azo-\(\beta\)-naphthol,

\[ \text{C}_6\text{H}_4\left\{ \text{SO}_3\text{Na} \right\} \]

\[ \text{N} : \text{N} \cdot \text{C}_6\text{H}_3\text{N} : \text{N} \cdot (1)\text{C}_10\text{H}_4\text{OH} \]

Ponceau 4 R. B.—Sodium salt of sulphobenzene-azo-benzene-\(\beta\)-naphthol-monosulphonic acid,

\[ \begin{align*}
\text{C}_6\text{H}_4\left\{ \text{SO}_3\text{Na} \right\} \\
\left\{ \text{N} : \text{N} \cdot \text{C}_6\text{H}_4\text{N} : \text{N} \cdot (1)\text{C}_10\text{H}_4\text{OH} \right\} \\
\left\{ \text{SO}_3\text{Na} \right\}
\end{align*} \]

Bordeaux G.—Sodium salt of sulphotoluene-azo-toluene-azo-\(\beta\)-naphthol-\(\beta\)-sulphonic acid,

\[ \begin{align*}
\text{C}_6\text{H}_3\left\{ \text{SO}_3\text{Na} \right\} \\
\left\{ \text{N} : \text{N} \cdot \text{C}_6\text{H}_3\text{N} : \text{N} \cdot (1)\text{C}_10\text{H}_5\text{OH} \right\} \\
\left\{ \text{SO}_3\text{Na} \right\}
\end{align*} \]

Naphthol Black 6 B.—Sodium salt of disulphonaphthalene-azo-\(\alpha\)-naphthalene-azo-\(\beta\)-naphthol disulphonic acid,

\[ \begin{align*}
\text{C}_{10}\text{H}_6\left\{ \text{SO}_3\text{Na} \right\}_2 \\
\left\{ \text{N} : \text{N} \cdot (4)\text{C}_{10}\text{H}_6(1)\text{N} : \text{N} \cdot (1)\text{C}_{10}\text{H}_4\text{OH} \right\} \\
\left\{ \text{SO}_3\text{Na} \right\}_2 \\
\left\{ \text{SO}_3\text{Na} \right\}
\end{align*} \]

Acid Brown G.—Sodium salt of benzene-azo-phenylene diamine-azo-benzene-p.-sulphonic acid,

\[ \begin{align*}
\text{C}_6\text{H}_5\text{N} : \text{N} \cdot \text{C}_6\text{H}_2\left\{ \text{NH}_2 \\
\text{N} : \text{N} \cdot (1)\text{C}_6\text{H}_4(4)\text{SO}_3\text{Na} \right\}
\end{align*} \]
CLASSIFICATION OF ARTIFICIAL COLOURING-MATTERS.

Cloth Brown G.—Sodium salt of diphenyl-disazo-dioxy-naphthalene-salicylic acid,

\[ (1)\text{C}_6\text{H}_4(4)\text{N} : \text{N} \cdot \text{C}_6\text{H}_3(1)\text{OH} \]
\[ (1)\text{C}_6\text{H}_4(4)\text{N} : \text{N} \cdot (\text{1} \cdot \text{C}_{10}\text{H}_5)\text{(7)OH} \]

Diamine Fast Red.—Sodium salt of diphenyl-disazo-salicylic-amido-naphthol-sulphonic acid,

\[ \text{C}_6\text{H}_4(4)\text{N} : \text{N} \cdot \text{C}_{10}\text{H}_5\text{(8)OH} \]
\[ \text{C}_6\text{H}_4(4)\text{N} : \text{NC}_6\text{H}_3\text{(10OH} \]
\[ \text{C}_6\text{H}_4(4)\text{N} : (6)\text{SO}_3\text{Na} \]

Benzopurpurine 4 B.—Sodium salt of ditolyl-disazo-binaphthionic acid,

\[ \text{C}_6\text{H}_3(3)\text{CH}_3 \]
\[ \text{C}_6\text{H}_3(4)\text{N} : \text{N} \cdot (\text{2} \cdot \text{C}_{10}\text{H}_5)\text{(1)NH}_3 \]
\[ \text{C}_6\text{H}_3(3)\text{CH}_3 \]
\[ \text{C}_6\text{H}_3(4)\text{N} : \text{N} \cdot (\text{2} \cdot \text{C}_{10}\text{H}_5)\text{(4)SO}_3\text{Na} \]

Closely related to the tetrazo colours are the derivatives of the thiotoluidines, of which the following two members are the most important:

Primuline is a mixture of which the chief constituent is

\[ \text{C} \left\langle \text{S} \right\rangle \text{C}_6\text{H}_3\text{C} \left\langle \text{S} \right\rangle \text{C}_6\text{H}_3\text{CH}_3 \]
\[ \text{C}_6\text{H}_3\left\langle \text{S} \right\rangle \text{C} \cdot \text{C}_6\text{H}_3\left\langle \text{SO}_3\text{Na} \right\rangle \]

Thioflavin-dimethyl-dihydrothiotoluidene-methyl chloride,

\[ \text{CH}_3\text{Cl} \]
\[ \text{C}_6\text{H}_3(4)\text{C}_6\text{H}_3 \left\langle \text{(1)C(4)C}_6\text{H}_4(1)\text{N(CH}_3)_2 \right\rangle \]

The precipitation of the members of this section is usually effected by the agency of barium chloride, which
forms the insoluble barium salt of the compound. In many cases, however, the number of lake-forming groups, in addition to the sulphonie-acid groups, renders it necessary to use further reagents to effect the complete precipitation of the colour, and to increase its fastness and brilliancy. This, and the formation of a series of pigments of growing importance, viz., the production of insoluble azo colours on suitable bases, will be more fully considered later.

*Nitroso and Iso-nitroso Colours.*—These form an unimportant group, from which lakes are rarely made. They contain the chromogen 'NOH. About the best-known member is Gambine, \( \beta \)-nitroso \( \alpha \)-naphthol

\[
\begin{align*}
C_7H_4 & \left(1\right) \text{CO} - C = \text{NOH} \\
& \left(2\right) \text{CH} = \text{CH}
\end{align*}
\]

*Oxyketone Colours.*—The oxyketone group is one of the most important, as it embraces the alizarines and allied colours, containing the powerful acid-forming chromogen, :CO, which, when acid-forming auxochromes are introduced into the molecule, gives powerful colouring-matters. These colours have, however, to be united to metallic oxides, before their full colouring power and shade are developed.

The derivatives of benzene and naphthalene are known, but they are of much less importance than those of anthracene, the principal colouring-matters derived from this hydrocarbon being—

Alizarine VI.—\( \alpha \)-\( \beta \)-dihydroxy-anthraquinone,

\[
C_7H_4 \left(\begin{array}{c}
\text{CO} \\
\text{CO}
\end{array}\right) C_6H_2\text{OH} \quad \left(6\right)
\]

Alizarine RG.—Trihydroxy-anthraquinone,

\[
\begin{align*}
HOC_7H_3 & \left(\begin{array}{c}
\text{CO} \\
\text{CO}
\end{array}\right) C_6H_2\text{OH} \quad \left(6\right) \\
& \left(5\right)
\end{align*}
\]
Purpurin.—Trihydroxy-anthraquinone,

\[ C_6H_4 \backslash CO \backslash CO \backslash C_6H - \text{OH (6)} \]

Alizarine Bordeaux.—Tetrahydroxy-anthraquinone,

\[ \text{OH} \quad \text{O} \quad \text{OH} \]

Alizarine Orange.—Nitro-alizarine,

\[ C_6H_4 \backslash CO \backslash CO \backslash C_6H \{ \text{OH (6)} \}
\]

Alizarine WS.—Sodium salt of alizarine-monosulphonic-acid,

\[ C_6H_4 \backslash CO \backslash CO \backslash C_6H \{ \text{OH (6)} \}
\]

Alizarine Blue.—Dihydroxy-anthraquinone-quinoline,

\[ C_6H_4 \backslash CO \backslash CO \backslash C_6H \{ \text{N = CH} \}
\]

Alizarine Indigo Blue.—The sodium bisulphite compound of pentahydroxy-anthraquinone-quinoline.

Great care has to be exercised in making lakes from these colours. The aluminium lakes are usually those prepared, and the author has found the following general method of procedure yield the most satisfactory results as regards brilliancy of shade:

Dissolve the alizarine in a mixture of carbonate and phosphate of soda, add the requisite quantity of oil, and carefully precipitate in the cold with sulphate of alumminium; add the calculated amount of acetate of calcium, and develop the shade by slowly raising to the boil in the course of about three hours, and boil one hour.

The reasons for this procedure will be fully explained.
when dealing with the precipitation of colours, since there are many points into which it would be inadvisable to go fully at this stage.

This method is also applicable to colours which are not alizarines, but, though belonging to other groups, are adjective colours.

*Ketonimides and Hydrazides.*—The ketonimides and the hydrazides are allied to the oxyketones, but only one colour of each group is at present of any interest to lake manufacturers, namely, Auramine, a valuable yellow basic dyestuff of great value in the production of green lakes from basic colours, and Tartrazine.

The chromophor of Auramine is \( \text{HN} : \text{C} \), and the generally accepted formula \( \text{HN} : \left( \text{C}_6\text{H}_4\cdot\text{N(Ch}_3\text{)}_2\right)\text{HCl} \)

This colour is precipitated with tartar emetic and tannic acid, as well as by the other methods used in the precipitation of basic colours; and finds its greatest use in lake-making as an agent for modifying the tones of the more powerful triphenylanine colours.

The hydrazine colour, Tartrazine, is the sodium salt of benzene azo pyrazaline-carboxy-disulphonic acid,

\[
\text{C}_6\text{H}_4(\text{SO}_3\text{Na}) - \text{N} - \text{COOH} \\
\text{N} - \text{CO} - \text{CH} - \text{N}_2 - \text{C}_6\text{H}_4(\text{SO}_3\text{Na})
\]

It precipitates completely with barium chloride, yielding, especially on a base of aluminium hydrate, a bright golden yellow lake; but, since cheaper colours give a very similar shade, it is not much used, though its lake is fairly fast.

*Triphenylanine Colours.*—In this group occur nearly all the basic artificial colouring-matters. They are usually very soluble, and of great colouring power, and, owing to the brilliant shades they produce, are largely used in the pro-
duction of lakes. They are, however, as a general rule, extremely fugitive to light, but their brilliancy causes them to be more in demand than faster colours which are duller in shade.

Like the azo colours, they can be divided into three classes:

(a) The rosaniline dyestuffs, containing the chromogen
\[ \equiv C—\text{NH—} \]

(b) The rosolic acid dyestuffs, containing the chromogen
\[ \equiv C—\text{O—} \]

(c) The phthaleins, containing the chromogen
\[ \text{C—CO—} \]

The following will be found to be representative members of the rosaniline dyestuffs:

- Malachite Green.—Zinc double chloride of tetramethyl-p-amidotriphenylearbinol,
  \[ \text{C}_6\text{H}_5—\text{C}—(1)\text{C}_6\text{H}_4(4)\text{N}’(\text{CH}_3)_2(1)\text{C}_6\text{H}_4(4)\text{N}’(\text{CH}_3)_2\text{Cl} \]

Brilliant Green.—Sulphate of tetraethyl-diamido-triphenylearbinol,
  \[ \text{C}_6\text{H}_5—\text{C}—(1)\text{C}_6\text{H}_4(4)\text{N}’(\text{C}_2\text{H}_5)_2(1)\text{C}_6\text{H}_4(4)\text{N}’(\text{C}_2\text{H}_5)_2 \]

Acid Green.—Sodium salt dimethyl-dibenzyl-diamido-triphenylearbinol-trisulphonic acid,
  \[ (1)\text{C}_6\text{H}_4(4)\text{N}(\text{CH}_2)\text{CH}_2\text{C}_6\text{H}_4\text{SO}_3\text{Na} \]
  \[ \text{HO—C—C}_6\text{H}_4\text{SO}_3\text{Na} \]
  \[ (1)\text{C}_6\text{H}_4(4)\text{N}(\text{CH}_2)\text{CH}_2\text{C}_6\text{H}_4\text{SO}_3\text{Na} \]

Guinea Green B.—Sodium salt of diethyl-dibenzyl-diamido-triphenylearbinol-disulphonic acid.
Night Blue.—Hydrochloride of p-tolyltetraethyl-triamidodiphenyl-a-naphthylcarbinol,
\[ C_6H_4N(C_7H_7)_2 \]
\[ C_6H_4N(C_2H_5)_2 \]
\[ C_10H_6N : (C_7H_7)HCl \]

Magenta.—The various brands of this colour are mixtures of the various salts of rosaniline and pararosaniline. The hydrochlorides may be expressed thus—

\[ C_6H_4N(3)CH_3 \]
\[ C_6H_4(4)NH_2 \]
\[ C_6H_4(4)NHC_6H_5 \]
\[ C_6H_4(4)NHC,H_4SO_3Na \]

Alkali Blue D.—Sodium salt of triphenyl-pararosaniline monosulphonic acid,

\[ C_6H_4(4)NHC_6H_5 \]
\[ C_6H_4(4)NHC,H_4SO_3Na \]

Methyl Blue C.—Sodium salt of triphenyl-pararosaniline trisulphonic acid,

\[ C_6H_4(4)NH\cdot C_6H_4\cdot SO_3Na \]

The basic dyestuffs of this group lend themselves to precipitation by various acids, such as tannic, oleic, phosphoric, and arsenious acids, producing lakes of varying stability and brilliancy. The most permanent are those produced from tannic acid, but they are far from being so brilliant, especially in the case of the magenta and green colours, as those produced by arsenious and oleic acids. The violets give the best results with phosphoric acid, which will not take down at all many of the blues and greens. Very good shades are produced with tannic acid from the blues and the bluish-greens.

Where the sulphinic-acid groups are not numerous,
the colour can often be treated as a purely basic one; but where they are numerous, means have to be taken, which will be more fully dealt with in a later chapter, to produce the double lakes.

Many of the acid colours, such as acid magenta, are of but little value to lake-makers, it being almost impossible to precipitate them suitably.

The colours from rosolic acid are not of very much importance, the chief representatives being—

Aurine or rosolic acid,

\[
\begin{align*}
&\text{C} - (1)C_6H_4OH (4) \\
&\text{C} - (1)C_6H_4OH (4) \\
&\text{C} - (1)C_6H_2O (4)
\end{align*}
\]

and Chrome Violet—sodium salt of aurine tricarboxylic acid,

\[
\begin{align*}
&\text{HO} -\text{C} - (1)C_6H_3COONa \\
&\text{HO} -\text{C} - (1)C_6H_3COONa \\
&\text{HO} -\text{C} - (1)C_6H_2COONa
\end{align*}
\]

neither of which find any employment in the production of lakes.

The phthalein colours, however, contain a very important class of colouring-matters, namely, the eosines, which, together with the basic colours derived from this group, the rhodamines, give a number of colours which yield lakes of the brightest and most brilliant shades. The general formula of the principal members may be represented by the following examples:—

Eosine A.—Alkali salts of tetrabrom-fluoresceine,

\[
(4) \text{O} : C_6HBr_2\left\langle\begin{array}{c}O \\ C \end{array}\right\rangle C_6HBr_2ONa (4) \\
C_6H_4COONa
\]
Erythrosine.—Alkali salts of tetraiodo-fluoresceïne,

$$\text{(4) O : } C_6\text{HI}_2\text{O}^\circ\text{C} \text{C}_6\text{HI}_2\text{ONa (4)}$$

$$C_6\text{H}_4\text{COONa}$$

Phloxin.—Alkali salts of tetrabromdichlor-fluoresceïne,

$$\text{(4) O : } C_6\text{HBr}_2\text{O}^\circ\text{C} \text{C}_6\text{HBr}_2\text{ONa (4)}$$

$$C_6\text{H}_2\text{Cl}_2\text{COONa}$$

Rose Bengal.—Alkaline salts of tetraiododichlor-fluoresceïne,

$$\text{(4) O : } C_6\text{HI}_2\text{O}^\circ\text{C} \text{C}_6\text{HI}_2\text{ONa (4)}$$

$$C_6\text{H}_2\text{Cl}_2\text{COONa}$$

Rhodamine B.—Hydrochloride of diethyl m. amidophthalein,

$$\text{(CH}_3\text{)}_2\text{N(4)C}_6\text{H}_3\text{O}^\circ\text{C} \text{C}_6\text{H}_3(4)\text{N(CH}_3\text{)}_2\text{HCl}$$

$$O = C \quad \text{C}_6\text{H}_4$$

Rhodamine S.—Hydrochloride of dimethyl m. amido-succineïne,

$$\text{(CH}_3\text{)}_2\text{N(4)C}_6\text{H}_3\text{O}^\circ\text{C} \text{C}_6\text{H}_3(4)\text{N(CH}_3\text{)}_2\text{HCl}$$

$$O = C \quad \text{C}_2\text{H}_4$$

Other higher products of this group, such as Galleïne and Coeruleïne, are of more interest to the dyer, producing violet and green shades on mordanted goods, but are rarely used in lake-making.

Azines, Oxazines, and Thioazines.—The oxazine, thiaoazine, and azine colours are the derivatives of a rather
complex chromophor, which, in the case of the oxazines, may be shown as follows:

\[
\begin{array}{c}
\text{N} \\
\text{O}
\end{array}
\]

the thio- or sulphur-azines, as

\[
\begin{array}{c}
\text{N} \\
\text{S}
\end{array}
\]

and the azines, as \( \begin{array}{c} \text{N} \\ \text{N} \end{array} \). In the safranines the latter become modified thus, \( \begin{array}{c} \text{N} \\ \text{N} \end{array} \). This group contains a number of extremely valuable colouring-matters, mostly of a basic character, which give very useful lakes, the principal being—

Fast Blue 2 B.—Chloride of dimethyl-phenyl-ammonium-β-naphthoxazine,

\[
\text{Cl}(\text{CH}_3)_2\text{NC}_6\text{H}_3\text{N}(\text{O})\text{C}_{10}\text{H}_6
\]

Nile Blue A.—Chloride of dimethyl-phenyl-ammonium-α-amido-β-naphthoxazine, \[
\text{Cl}(\text{CH}_3)_2\text{NC}_6\text{H}_3\text{N}(\text{O})\text{C}_{10}\text{H}_5\text{NH}_2
\]

Methylene-Blue B.—Chlorides of tetramethyl thionine,

\[
\text{N}(\text{CH}_3)_2
\]

New Methylene-Blue.—Chloride of diethyl-toluthionine,

\[
\text{ClH}(\text{C}_2\text{H}_3)_2\text{N}^\text{NC}_6\text{H}_2\text{S}^\text{NC}_6\text{H}_2\text{ClNHC}_2\text{H}_5
\]
Of the azines, the safranines are of the greatest interest. The indulines, though yielding lakes, are not much used by the lake-makers, since the shades produced are lacking in brilliancy, and can more readily be obtained from other colours.

The general formation of the safranine group will be understood from the following examples. These colours are basic in nature, and give very good results with tartar emetic and tannic acid.

Safranine B.—Diamido-phenyl-phenazonium chloride,

\[ \text{H}_2\text{NC}_6\text{H}_3\left(\text{C}_6\text{H}_3\text{NH}_2\right)\text{ClC}_6\text{H}_3 \]

Basle Blue R. — Dimethyl-amido-tolylamido-tolylphenonnapthazarine chloride,

\[ (\text{CH}_3)_2: \text{N-C}_6\text{H}_3\left(\text{CH}_3\text{H}_2\text{NHC}_6\text{H}_2\right)\text{ClC}_6\text{H}_3 \]

Metaphenylene-Blue.—Tetramethyl-diamido-o-tolyl-diphenyl-azonium chloride,

\[
\begin{array}{c}
\text{ClC}_6\text{H}_3 & \text{ClC}_6\text{H}_3 \\
\text{C}_6\text{H}_3 & \text{C}_6\text{H}_3 \\
\text{N(CH}_3)_2 & \text{N(CH}_3)_2
\end{array}
\]

The tannic acid lakes of these colours are the best. The blues yield fine shades; the red shades yield brighter and faster lakes than those produced from magenta, and are of great use in the production of bright maroon lakes, as they have not the same tendency to darken. The quinoline and acridine colours are principally of inter-
est because they yield us Quinoline Yellow and the Phosphines. Quinoline, $C_9H_7N$, and acridine, $C_6H_4 \begin{array}{c} \text{CH} \\ -N \end{array} \text{CH}$, are the chromophoric groups; but their power is but feeble, and only becomes of value when powerful auxochrome groups are introduced.

Quinoline Yellow is the disulphonic acid of quinophthalone,

$$C_6H_4 \begin{array}{c} \text{CH} \\ \text{N} \end{array} C_9H_4N(SO_3Na)_2$$

and is entirely precipitated by barium chloride.

The acridine colours are basic. The Phosphines are used for tinting purposes, but do not by themselves give pleasing lakes; both tannic acid and resin soap take them down, the latter giving the brighter shades. By reference to the formula of Phosphine, nitrate of diamido-phenyl-acridine,

$$C_6H_4NH_2$$

$$C_6H_4 \begin{array}{c} \text{C} \\ \text{N} \end{array} C_9H_3NH_2 \cdot HNO_3$$

their general constitution can easily be understood.

Of recent progress in the dye industry, the introduction of the azo colours and the development of the vat dyes are of interest to the pigment-maker. Sulpho and indoanthene colours are not of great value to commercial lake manufacturers, for, though they can be applied, the dullness of the resulting lakes prevents their adoption in place of much brighter shades, whose durability is sufficient for the purpose for which they are manufactured. Some of these colours have, however, replaced the more fugitive
basic dyes in stencil inks and other similar spirit preparations.

Of the groups of artificial colours those described will be found to contain the colours most generally used in the production of lakes. Those which have been dealt with but slightly contain many valuable colours, but they are of more interest to the dyer and colour-maker, being only very occasionally applied to the production of pigments. It is for the latter reason that many groups have been omitted entirely, and not because they are considered unimportant.
CHAPTER III.

THE NATURE AND MANIPULATION OF ARTIFICIAL COLOURS.

The colours derived from coal-tar come into the market in three forms, namely—

I. Amorphous powders.

II. Crystals.

III. Pastes.

By far the greater number are sold as amorphous powders. The crystalline variety are mainly basic colours, such as magenta, ethyl-green crystals, violet crystals, etc., and can generally be regarded as almost pure derivatives of the dyes.

The colours which are sold as powders are often diluted with from 10 per cent. to 80 per cent. of soluble matter, such as dextrin, common salt, Glauber's salts, and similar bodies. There are several reasons for this adulteration, the chief being the reduction of the strength of the colour, so that larger quantities of the dyestuff can be used and the approximation of the price to that of competing colours. By this means the danger of a slight error in weight causing a considerable alteration in the shade of a pigment is avoided. These colours, it must be remembered, are produced and prepared for the market for the use of dyers and printers, and the adulterants added may, for many reasons, render the colours more suitable for use in the dye-house; but, when used for the production of lake pigments, by entering into one or more of the reactions (29)
taking place in the formation of the lake, they may lead to results that are not expected, and may cause a colour, otherwise admirably adapted for this purpose, to be condemned. It is therefore advisable, wherever practicable, to obtain as pure a colouring-matter as possible. The lake-maker makes use only of the tinctorial power of the colours, diluting the shade produced, by means of bases, to the depth and strength required, and the presence of diluents, if they enter into any reaction during the lake-forming process, leads not only to misleading results but actually increases the cost of production. The purer brands of dyestuffs are often distinguished by the term extra, and though the price of the latter may be from six to ten times the price of the ordinary brand, it will be found that value for value the purer form works out much the cheaper in practice.

The paste colours as a rule are those insoluble or nearly insoluble in water, *e.g.*, the various alizarines or pigment colours, Lithol Red R, Lake Red P, etc. They usually contain 20 per cent. of colouring-matter. In many, but not all instances, colours so supplied can be obtained almost pure in powder form, and it is better for the reasons already stated to use the latter where possible. With the colours of the azo group, however, and especially with those which require no addition to bring up the shade, but are simply ground or mixed with the base or filler, better results are obtained by using them in paste form since the colour is then more readily and intimately mixed with the substrata. The lake-maker must discriminate in these cases as to which form will prove most economical in use.

In selecting colours it is advisable to buy only from the actual makers or their immediate agents, avoiding as far as possible merchants and dealers. The colours
obtained from the latter cannot be relied upon to be constant in composition or purity; and should any cause for complaint arise it would be impossible to have it investigated by the dye manufacturer, since he cannot be responsible for what may have happened to his products whilst passing through various hands after leaving his factory.

It is not possible in the present condition of the dye industry to particularize the most suitable products of these firms. Many of them are handicapped by the prevailing conditions, and have not had the time and opportunity to develop the colours used in lake-making on the lines they would wish. It is, however, to be hoped that these products will be given every opportunity of replacing the continental colours. The lake manufacturer should not hesitate to point out any defects and to request the dye-stuff-makers to correct, if possible, those properties of their dyestuffs which render them inferior to those obtained from the previous sources of supply. It is to be feared that for a little time the greatest consideration will be necessary on both sides, before the products of the comparatively new British dye industry can be accepted with the same reliance as were those of the great German dye manufacturing companies. But there is no reason why in a comparatively short time the British products should not inspire confidence as great as, if not greater than, those previously obtained from Germany.

In the case of many of the colours made by the British firms before the war, there is no doubt that the shades had not the brilliancy of the same material made abroad. This would not have been so fatal to the use of the British colour, had not the price been almost without exception, higher, and in keenly cut prices the lake manufacturer could not afford to pay the higher cost.
The manufacture of lake pigments.

The suitability of a dyestuff for its application to textile fabrics is no criterion of its suitability for lake-making, and it is only by repeated trials and experiments that the value of a dyestuff for the latter purpose can be determined.

When colours are offered which do not bear the name of a recognized firm, they must always be looked upon with a certain amount of suspicion, since they are often sophisticated colours prepared for a special purpose, and, as such, are of questionable value in lake-making. It is certain that there will be on the market many dyestuffs from small and experimenting firms at rates much lower than those obtaining for established brands, and, while these may be used for odd lots of lake pigments, it would not be advisable for a lake-maker to attempt to prepare his standard shades and products from them. Great care and discretion will have to be employed in their use.

Colours should always be dissolved in water separately, and then sieved into the precipitating tank through a fine sieve, about eighty meshes to the inch. The wooden vessels in which acid and basic colours are dissolved should not be used for either class of dyestuff, since if the strong basic colours come into contact, even in minute quantities, with acid colouring-matters, they frequently alter materially the shade of the finished lake, or, worse still, produce dark tarry specks throughout the pigment, absolutely ruining it for all ordinary processes.

Where a mixture of similar colours is being used, it will be found that if the colours are dissolved and added separately to the tank, a different shade is produced from that obtained when all the colours are mixed together before addition. In the case of azo-acid colours, the latter is the more correct procedure, but with basic dyes it is, as
PLATE 1

Manufacture of Lake Pigments

To face page 32
a rule, preferable to adhere to the former since, should one member of a mixture contain an acid group, another will frequently react with it, producing a tarry precipitate with which it is difficult to deal.

Plate I illustrates some of these points:—

(1) Shows the lake produced from Scarlet R (Brit. Dyes) on the clay alumina base by barium chloride.

(2) A similar lake produced from Orange WH (Brit. Dyes).

(3) A similar lake produced from a mixture of equal parts of Scarlet R (B.D.) and Orange WH (B.D.) dissolved together.

(4) A similar lake to No. 3, but the dyestuffs dissolved separately.

(5) A lake produced on the clay alumina base by dissolving and adding separately Scarlet R (B.D.) and Magenta Crystals (B.D.), and precipitating the whole with barium chloride.

(6) The same lake as No. 5 but the Scarlet R and Magenta dissolved together.

In the majority of cases the best mode of dissolving the artificial colours is to make them into a thin cream with just warm water, and then add boiling water until the colour is entirely dissolved. Though boiling the colours does not usually injure them, it is better avoided, since, in some cases, notably in that of auramine, the colour is decomposed, giving quite a different shade from that expected.

In the case of colours obtained in the crystalline form a slightly different procedure is advisable, viz., to add them little by little to a considerable quantity of nearly boiling water, in the proportion, say, of half a pound of colour to 2 gallons of water, agitating until solution is complete.

Except in the case of difficultly soluble colours, the addition of soda or other materials to the water, in order to facilitate solution, is to be strongly deprecated, since such additions are the cause of difficulties which would
otherwise be avoided. In such cases, however, the addition of a little glycerine to the dyestuff when making it into a cream with water greatly increases the solubility. An equally effective but cheaper aid to solution is a small quantity of neutral Turkey Red Oil. Care, however, is required in using this, for, if in the subsequent manufacturing operations there be any considerable effervescence, as when soda ash is added to aluminium sulphate, the mixture will froth excessively, thereby lengthening the sticking time, and giving much unnecessary work and trouble.
CHAPTER IV.
LAKE-FORMING BODIES FOR ACID COLOURS.

Having considered the general constitution of the artificial colouring-matters, it is advisable to enter into the chemistry and nature of those reagents commonly used in the commercial production of lake pigments. There are many methods, extremely interesting from a scientific point of view, of forming lakes; but attempts to reduce them to practice fail, because either they are too expensive, or the results are not of sufficient value to induce deviation from more general methods.

The principal materials used in the preparation of lakes from acid dyes are the salts of—

Barium—-the chloride.
Lead—-the nitrate and acetate.
Zinc—-the sulphate.
Aluminium—-the sulphate, potash alum, and acetate.
Tin—-the chloride.
Antimony—-the chloride.
Calcium—-the nitrate, acetate, and phosphate.
Sodium—-the phosphate.

Barium chloride is the typical lake-forming body for sulphonic acids, forming the barium sulphonates which, in the greater number of cases, are insoluble in water. It is usually sold in the form of crystals, which are colourless rhombic prisms containing two molecules of water of crystallization, having the formula $\text{BaCl}_2\cdot2\text{H}_2\text{O}$, molecular
The manufacture of lake pigments.

The crystals are soluble in approximately twice their weight of boiling water. They lose their water of crystallization if heated to 113° C., fuse at a red heat, and, when fused in the presence of air, lose chlorine with the formation of baryta: consequently the fused varieties have often an alkaline reaction.

Barium chloride is made by dissolving witherite, natural carbonate of barium, in hydrochloric acid, or, by fusing barytes with carbon, limestone, and calcium chloride, lixiviating the resulting mass with water to dissolve out the chloride, and crystallizing the solution so obtained.

A good sample should, in mass, appear almost pure white, and a single crystal should appear clear and transparent. On no account should it contain any iron salts, which will give a brownish hue to the bulk, and are easily detected by the bluish coloration obtained by the addition of a little ferrocyanide solution to a solution of the chloride. It should not feel damp to the touch, but quite dry. Free acid should not be present, or it will play havoc with the colours in course of manufacture. Barium chloride must be carefully handled, since, taken internally, it is a very violent poison; and its solutions coming in contact with sores cause them often to ulcerate slightly, and their healing to be protracted.

Caustic baryta, Ba(OH)₂, is used occasionally in the production of lakes, in order to procure the entire precipitation of colours containing hydroxy groups, which, owing to their weak acid property, are unable to decompose barium chloride. It is soluble in water to the extent of 3·5 parts in 100 parts of cold and 90·2 of hot. Caustic baryta rapidly absorbs carbon dioxide, and has a strong alkaline reaction. As indicated, it is only used in special cases, and is not as a rule found in the lake-maker's store.
Nitrate of lead, \( \text{Pb(NO}_3\text{)}_2 \cdot 2\text{H}_2\text{O} \), molecular weight 366.1, crystallizes in regular octohedrons and is fairly soluble, dissolving in approximately its own weight of water.

Acetate of lead, \( \text{Pb(CH}_3\text{COO)}_2 \cdot 3\text{H}_2\text{O} \), molecular weight 378, is extremely soluble, dissolving in eight times its own weight of cold water, and in its water of crystallization at 75.5° C. It crystallizes in oblique rhombic prisms, and on exposure effloresces. From its sweet astringent taste it has obtained the name of sugar of lead which comes into the market in two brands—brown and white. For lake manufacture the brown variety may be used,—it is a little cheaper than the white,—but its use is not to be recommended for high-class colours. White sugar of lead of good quality should be perfectly white in appearance, and the crystals should be of fairly large size. There are some qualities very white in appearance, and finely crystalline: these do not work well, giving rise to excessive frothing, and, where the colours are used in size, causing often very considerable annoyance by being responsible for the lake rising and running over the machine. As with barium chloride, the salt should be perfectly dry to the touch.

The dibasic and tribasic acetates of lead, made by heating litharge with normal lead acetate, are of great use in dealing with some hydroxy compounds.

It is, however, much cheaper for the lake manufacturer to make his own nitrate and acetate of lead. They can be made from either white lead or litharge. White lead can readily be obtained in the form of a pulp containing 15 to 20 per cent. of water. It works out slightly dearer than litharge, but dissolves more readily and with less labour than the latter in nitric acid, and when used in slight excess ensures the absence of free acid. Lead nitrate
so prepared can be kept in a solution of known strength, thus saving the time and expense incurred in dissolving the crystallized salt.

The normal and basic acetates are most conveniently prepared from litharge and acetic acid. Ground litharge is not suitable since the action between the fine oxide and acid proceeds very rapidly with the evolution of heat, causing the ground litharge to set into hard lumps of a mixture of litharge and insoluble basic acetate. The best method of procedure is to run into an approximately 10 per cent. solution of acetic acid, at 30° C., the calculated amount of litharge required to produce the normal salt, roughly 2 cwt. of litharge to 120 lb. of pure acetic acid, stirring vigorously throughout the addition. If the litharge be added too rapidly, the basic salt separates out with the litharge and solution is not readily completed; in addition, excessive rise in temperature results in loss of acetic acid by evaporation. When properly made and the proportions given carefully adhered to, a solution of the normal acetate free from basic acetate is obtained.

The basic salts are obtained by the addition of the calculated amount of litharge slowly and with continual stirring, the normal acetate taking up the lead oxide fairly rapidly at first and then more slowly as it approaches saturation as tribasic acetate.

Lead salts possess the power of precipitating a large number of dyestuffs, both sulphonic acids and triphenylmethylene colours; but, save for eosines and allied colours, their use is not to be advised, since, apart from being far more expensive than barium salts, the pigments given are, as a rule, much duller than those produced by other precipitating agents. In cases where they are suitable, however, they demonstrate their suitability in no doubtful way.
In some cases the precipitation is much more complete with acetate of lead than with barium chloride, due mainly, in all probability, to acetic acid being a much weaker acid than the hydrochloric of the barium salt. In any case, where there is simultaneous precipitation of an insoluble sulphate, the use of lead salts, which are from three to four times more expensive than barium chloride, would cause such an increase in the cost of production that their use is prohibited. Lead sulphate is much more soluble in water than barium sulphate, and very readily soluble in solutions of certain salts, especially acetates, and this fact must always be borne in mind when dealing with this compound of lead in lake manufacture. Yet, as will be seen, since the brightest of the lakes obtained from azo-sulphonic acid colours are produced by such methods, it is perhaps better to retain the use of lead salts simply in those few colours for which it is undoubtedly the best pigment-forming agent, and which, as a general rule, are thrown down on inert bases.

The two salts of lead which are used for this purpose are the acetate and nitrate. The nitrate is considerably cheaper than the acetate, and can in many cases be substituted for the latter; but, where the question of the difference in price between the two can be neglected, the use of the acetate is to be preferred, because, should free nitric acid be liberated during the reaction, its powerful action on the colouring-matter causes great differences in shade.

Of the compounds of antimony the most familiar is potassium antimonyl tartrate, better known as tartar emetic, \( \text{C}_4\text{H}_4\text{O}_6(\text{SbO})\text{K} + \text{H}_2\text{O} \). It forms rhombic prisms, soluble at the ordinary temperature in about 15 parts, and at the boil in about 3 parts of water. When heated to
200° to 220° C., it loses water, and forms \( \text{C}_4\text{H}_2\text{O}_6\text{SbK} \), which on solution reforms tartar emetic. Whether this compound can be regarded as a simple tartrate or not is doubtful; evidence tends to show that it should be regarded as the potassium salt of a peculiar acid, having the following constitution:

\[
\text{C}_2\text{H}_2(\text{OH})_2\left(\text{CO} \cdot \text{O}\right)\text{SbOH}
\]

Tartar emetic is largely used, both in dyeing and lake-making, for fixing lakes produced from basic colours by means of tannic acid. In the preparation of lakes, it is usually added before the tannic acid. In many cases it will be noticed that a slight precipitation takes place, which is, in all probability, caused by the combination of the basic groups in the colouring-matter with the hydroxy groups of the tartaric acid. The lakes produced by its means with tannic acid are by far the most permanent; and when tannic acid is used no fixing agent other than tartar emetic should be employed, for, of all tannic acid lakes, they are the brightest and fastest.

The oxide of antimony, \( \text{Sb}_2\text{O}_3 \), is used in the same way as white arsenic in the precipitation of basic colours, by dissolving it in sodium carbonate, and precipitating the lake and the base together by the addition of the solution to a solution of aluminium sulphate and the colour. It is, however, but little used for this purpose.

Zinc sulphate, \( \text{ZnSO}_4\cdot7\text{H}_2\text{O} \), white vitriol, is used in some cases to precipitate eosines, but its application is limited. It is a white crystalline solid, fairly soluble in water, and is decomposed by the action of normal sodium carbonate into basic carbonates, and zinc hydrate. In some instances, notably in that of the Marine Blue of
ML, B, and the Erioglaucines, a small percentage of the mixed carbonate and hydrate so produced, mixed with the base, leads to much more complete precipitation of the colouring-matters than would otherwise be obtained.

_Aлюминиум salts._—The salts of this metal, notably the sulphate and the acetate, are by far the most important reagents at the command of the lake-manufacturer. Their value does not lie in their ready precipitation of the colouring-matters, since, with very few exceptions, the addition of an aluminium salt to the solution of a colouring-matter produces no apparent change, but in the fact that they form a source of aluminium hydrate, Al₂(OH)₆. The latter can act either as an acid or basic substance according to conditions, and in consequence of this property is able to play the part of a powerful auxiliary in the precipitation of colouring-matters, and to combine with other bodies giving insoluble aluminium compounds, which are an important class of lake bases.

_Aлюминиум сульфат, Al₂(SO₄)₃H₂O._—This salt is extremely soluble in water and comes into the market in various forms, very rarely crystalline. It is usually sold as guaranteed to contain a certain percentage of Al₂O₃. Lump aluminium sulphate usually contains from 11 to 16 per cent. of Al₂O₃; but this quality is apt to contain a considerable quantity of iron. The best make is a fine dry white powder, containing about 17 per cent. of Al₂O₃; this, and this alone, should be used in the manufacture of pigments, since it is much purer and more reliable than other qualities having very little difference in price to recommend them.

The best guides to the selection of a sulphate of aluminium are—the colour, which should be quite white; the percentage Al₂O₃ content; and freedom from iron. The
The presence of 0.5 per cent. $\text{Fe}_2\text{O}_3$ is sufficient to render a brand utterly unsuitable for the production of alizarine lakes.

The salt has a strong acid reaction, and is decomposed by the action of sodium carbonate, thus—

$$\text{Al}_2\text{(SO}_4\text{)}_3 + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} = \text{Al}_2\text{(SO}_4\text{)}_2(\text{OH})_2 + \text{Na}_2\text{SO}_4 + \text{CO}_2$$

$$\text{Al}_2\text{(SO}_4\text{)}_2(\text{OH})_2 + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} = \text{Al}_2\text{SO}_4(\text{OH})_4 + \text{Na}_2\text{SO}_4 + \text{CO}_2$$

$$\text{Al}_2\text{SO}_4(\text{OH})_4 + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} = \text{Al}_2(\text{OH})_6 + \text{Na}_2\text{SO}_4 + \text{CO}_2$$

If the solutions of sulphate and carbonate be very dilute and cold, no permanent precipitation takes place until a considerable quantity of sodium carbonate has been added, since the basic sulphates formed do not separate at low temperatures. This property can be taken advantage of in producing pale aluminium lakes, by adding the colour, for example, methyl-violet B, to a solution of basic aluminium sulphate, and inducing complete precipitation of the aluminium hydrate by adding slowly the requisite amount of soda and raising the temperature. The basic sulphates of aluminium have a very considerable attraction for basic colouring-matters.

When the solutions of sodium carbonate and aluminium sulphate are hot and concentrated, the precipitate is generally very lumpy, and, if there be an excess of aluminium sulphate present, combination between the hydrate already formed and the excess takes place, giving the precipitate a semi-crystalline appearance.

The acetate of aluminium is in its chemical behaviour very similar to the sulphate, save that the basic salts are more stable than those of the latter. It is prepared, either by dissolving the hydrate in acetic acid, or by heating a solution of aluminium sulphate with sugar of lead.

It is of far greater importance in dyeing and calico
printing than in lake-making. In the latter industry it is only substituted for aluminium sulphate in those cases where the presence of sulphuric acid is objectionable.

Hydrate of aluminium, $\text{Al}_2(\text{OH})_6$—This body is produced when caustic soda or potash, ammonium hydrate or an alkaline carbonate is added to a solution of an aluminium salt; it is soluble in caustic alkalies, and is therefore usually precipitated by means of the carbonates.

When produced from cold dilute solutions, aluminium hydrate is of a transparent gelatinous nature, but, on heating, becomes opaque, and more contracted in bulk. If precipitated from hot solutions with ammonia, it is thrown down in the form of a light opaque precipitate. With carbonated alkalies the precipitate is much more dense, and is very lumpy, owing to the reaction being incomplete.

The form in which aluminium hydrate is brought into contact with colouring-matters determines largely the amount of colour with which it combines. Whether with hydroxy compounds the aluminium lake is more readily formed, or there is merely mechanical absorption, is a moot point; but the fact remains that the addition of a colour to aluminium hydrate produced in the cold, and subsequent boiling, fixes more colour than when the lake is produced hot from the same materials, or when the production of the aluminium hydrate itself takes place, in presence of the colour, in hot concentrated solutions.

When the colours are intended for dry pigments it is advisable to precipitate the aluminium hydrate from fairly concentrated solutions; otherwise the lakes dry very hard, instead of being friable.

Aluminium hydrate, when dried, forms a hard white horny substance, which has the composition $\text{Al}_2(\text{OH})_6$, and only on ignition is the whole of the water driven off,
leaving $\text{Al}_3\text{O}_3$. The conditions under which it is produced influence the nature of the dried substance, and a careful study of this point is very essential when producing lakes in which aluminium hydrate forms the greater part of the base. This is dealt with more fully in Chapter VI., under lake bases.

It occurs naturally as bauxite, and, when finely ground, forms a valuable filler in conjunction with the more dense minerals used for this purpose.

Of the tin salts, stannous chloride, $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$, which crystallizes in transparent monoclinic prisms, is the only compound used. It dissolves in its water of crystallization at $40^\circ$ C, is hygroscopic, and is only stable in concentrated solutions, decomposing on dilution, forming a basic chloride which is insoluble in water. This salt is but little used since its powerful reducing action destroys the shade of many of the artificial colours. It forms the basis, however, for the preparation of those stannic acid compounds used in the manufacture of special lakes from basic colours, especially greens and blues.

Calcium salts are not used as precipitating agents, but the acetate and nitrate are employed to introduce into certain lakes, e.g., the alizarine compounds, the calcium which is an essential factor in their composition: they can, in fact, be more properly regarded as assistants to the lake-forming bodies proper.

The necessity of employing calcium salts absolutely free from iron, in the manufacture of alizarine lakes, is very important. The author has found the following method of purification efficient. Dissolve the chalk, or any calcium salt, in hydrochloric acid; add a little chlorate of potash to oxidize any iron present, and then excess of disodium hydrogen phosphate, precipitating the mixture with excess
of ammonia. Wash the precipitate well by decantation with distilled water, and treat with acetic acid. This readily dissolves the calcium phosphate, leaving the iron and aluminium as insoluble phosphates. Filter and decant the clear solution which will be found quite free from any contamination with iron.

Sodium acetate, \( \text{CH}_3\text{COONa}_3\text{H}_2\text{O} \), is also largely used in lake manufacture. It is introduced into various mixtures for two reasons: firstly, because in presence of a free mineral acid it is decomposed with the liberation of acetic acid, which has but little action, in comparison with the stronger acids, on the various ingredients of a lake pigment; and secondly, its faint alkalinity in many cases enables the shade and brilliancy of the colour to be fully developed, this object not being attainable in the presence of free strong acid or alkali.

Sodium acetate crystallizes in monoclinic prisms, and is soluble in about half its weight of boiling water. A tartar emetic and tannic acid lake made in the presence of this salt settles readily: in its absence there is sometimes considerable difficulty in washing the lake thoroughly, since the pigment either remains in suspension or settles only very slowly.
CHAPTER V.

LAKE-FORMING BODIES FOR BASIC COLOURS.

Just as the acid colours behave as simple acids, so the basic colours act as simple bases, and it will be found that the lakes formed from basic colours are combinations of the latter with some acid or semi-acid body. The acids most commonly used for this purpose are tannic, phosphoric, arsenious, antimonious, stannic, resinic, and palmitic, stearic, and allied fatty acids.

The most important of these, in respect of producing the fastest and most satisfactory lakes, is—

Tannic acid, digallic acid.—Tannin, \( C_6H_2(OH)_3COOC_6 \)
\( \text{H}_2(OH)\text{COOH}, \) is a weak astringent acid substance derived from gall nuts, formed by the action of insects on certain trees and shrubs, and from sumach, the twigs and leaves of an Italian shrub, by extraction with water and alcohol. Its constitution may be expressed by the following formula:—

\[
\begin{align*}
\text{HO} & \xrightarrow{C_6H_2} \text{OH} \\
\text{HO} & \xrightarrow{C_6H_2} \text{CO} \\
\text{HO} & \xrightarrow{C_6H_2} \text{O} \\
\text{HO} & \xrightarrow{C_6H_2} \text{COOH}
\end{align*}
\]

Tannic acid is sold in various brands, containing more or less free acid. A good variety only should be used for the formation of pigments, and this should be of a pale yellowish-brown colour. It should be kept in closed
vessels, since under the action of air and light it undergoes considerable change.

In alkaline solutions tannic acid absorbs oxygen, darkening in colour. Its aqueous solutions are precipitated by dilute mineral acids, except nitric acid, and by sodium and potassium chloride and potassium acetate, but not by Glauber's salts.

It is a monobasic acid, decomposing carbonates, and forming, with various metallic oxides, insoluble salts.

Tannic acid is fairly expensive, and is used only for the purest shades of colour. It is customary for deep shades, in which the yellow or brownish tint imparted by the colouring-matter in the acid is not harmful, to use extracts of sumach derived from the twigs of several plants of the genus *Rhus*, the finest variety of which comes from Sicily, and of myrobalans the fruit of *Termatalia Chebula*, a tree common in India. For dark blues and greens, galls or extract of galls can be used with advantage.

Phosphoric acid, $\text{H}_3\text{PO}_4$.—Of the various acids of phosphorus only normal phosphoric acid is usually employed in the manufacture of pigments.

The free acid, however, is not employed as such but in the form of a salt known commercially as phosphate of soda, which is really disodium hydrogen phosphate, $\text{Na}_2\text{HPO}_4\cdot10\text{H}_2\text{O}$. This salt, when added to a solution of a basic dye, *e.g.*, Methyl Violet or a Rhodamine, does not precipitate the colouring-matter, unless the addition results in the formation of an insoluble phosphate at the same time. The latter is usually obtained from an aluminium salt.

Disodium hydrogen phosphate, though seemingly an acid salt, has a faintly alkaline reaction, and is readily soluble in water. When used for the production of the
insoluble phosphates of aluminium, calcium, or barium, it should be remembered that it is an acid salt, and free acid is often liberated during the precipitation. Nearly all the phosphates being readily soluble in dilute acids, precipitation under such conditions is not complete, and the resultant product is slimy, unfilterable, and unusable. If the solutions be rendered alkaline, complete precipitation is obtained, but the colour is almost entirely redissolved. When using disodium hydrogen phosphate it is advisable to add to it almost sufficient soda to neutralize any free acid that may be liberated, but the addition should not be sufficient to give an alkaline solution. The molecular weight of disodium hydrogen phosphate is 322, and it requires another atom of sodium to change it to the normal salt. This is contained in 53 of sodium carbonate, Na₂CO₃, and the addition, therefore, of soda ash to the extent of one-sixth the weight of disodium hydrogen phosphate used will give approximately the conditions required to prevent the formation of free acids. In this case the precipitation of the pigment takes place in the presence of a large excess of the precipitating agent, and therefore the calculation as to the quantity of precipitating agent required for the colour may be neglected, the only calculation being the quantity of colour required to give a given shade with a given quantity of base, or rather of materials about to be used.

Arsenious acid, H₃AsO₃.—The solution of arsenic trioxide in water yields a solution of this acid, which, however, is very unstable, although its salts are extremely stable. As with phosphoric acid, the sodium salts are used in the preparation of lakes.

These salts are not usually bought by the lake-manufacturer, but are prepared by him by dissolving white
arsenic or arsenic trioxide in sodium carbonate. Neither the normal nor the hydrogen salt effects any precipitation when added to a solution of a colouring-matter, say Ethylgreen Crystals (Ber), lake formation only taking place when an insoluble arsenite is precipitated in the presence of the colouring-matter; and it appears that the lake-forming properties of both this acid and phosphoric are exercised only when combined with some metal forming a complicated acid salt. Such are produced when solutions of the alkali salts of these acids are added to a solution of an aluminium salt, and it is to be assumed that these arsenical and phosphoric aluminium compounds fix the dye, the reaction being not one of simple precipitation by a polyhydroxy acid. This is confirmed by the fact that the addition of a colour to the thoroughly washed precipitate, formed by the interaction of a solution of aluminium sulphate, and an alkaline arsenite or phosphate, results in its fixation.

Great care must, however, be taken in the use of both these acids, so that at the completion of the reaction the supernatant liquor is neutral or very slightly acid; and, in dissolving arsenic trioxide in sodium carbonate, such amount of sodium carbonate must be used that, when the solution is added to the aluminium salt, these conditions are fulfilled. This, of course, entails a careful examination of the raw materials used, otherwise variable results will be obtained.

Stannic acid and meta-stannic acid are used for the preparation of lakes from basic colours, but owing to the feeble attraction of the latter for colours, its application is limited. Stannic compounds are used for the production of some green lakes which are more brilliant than the tannic acid greens, but not equal to those produced by arsenious acid, in view of their less poisonous character.
Stannous chloride, which decomposes into the basic salt, when added to some colours, precipitates them; the further addition of tannic acid deepens and renders the shade duller but faster.

Stannic chloride, on addition to basic colours in alkaline solutions, is decomposed into stannic hydrate, which is thrown down together with the tin lake, if the solution be not too strongly alkaline. The tin lakes require great care in their manipulation, and are rarely met with, although those prepared from natural colours, such as fustic, Persian berries, etc., are of considerable importance.

The acids of antimony are similar to, and are applied in the same way as, those of arsenic.

Colophony, or rosin, contains resinic acid, which dissolves very readily in sodium carbonate giving a solution of what is generally known as rosin soap. It is largely used to produce brilliant magenta and green lakes, by precipitating the basic colours in conjunction with a metallic resinate, such as the lead, zinc, or aluminium compound. The rosin lakes are nearly all soluble or apparently soluble in oils and varnishes, and the metallic resinates forming the matrix of the compound being transparent in oil if properly made, complete the appearance of solubility. They are certainly very brilliant, and have a considerable demand among wall-paper manufacturers. For stencil inks and tin printing the process adopted and the precautions to be observed are similar to those in the making of phosphoric and arsenical lakes; but for oil or lithographic work the rosin lakes are useless and are about the most fugitive lakes produced from basic colours.

The use of various fatty acids, in the form of soaps, except in conjunction with some other precipitating agent, is not to be recommended for throwing down basic colours;
but considerable use is made of these acids, both in the form of soaps, and as soluble preparations of the free acids, such as occur in the various sulphated and soluble oils, when amido-acid colours are being transformed into lake pigments, since their property of combining with the basic groups fixes the colour more completely, and gives brighter and clearer shades.

They must, however, be used in small quantities only, and with great discrimination and care; otherwise they are apt to make the colour bleed, causing a loss of colouring-matter and deterioration of the shade.

Sulphonated castor-oil, neutralized with ammonia, rather than soda, is of more importance as an assistant in the production of lakes than as an actual precipitant. It certainly combines with and precipitates colours, but the resultant lakes are unsatisfactory. Slight additions of this material to the lake, after the usual procedure has been carried through, not only, in many cases, completes the precipitation, but also modifies the precipitate in such a way as to facilitate its filtration and preparation for use, besides modifying it in other important particulars which are more fully dealt with in the next chapter.
CHAPTER VI.
LAKE BASES.

Hitherto the production of the lake proper has been dealt with, but in order to develop the full value of the colour, attain the maximum brilliancy of colour, and to impart to the pigment such physical properties as opacity, friability, covering power, and density, which are rarely if ever characteristics of the pure lake, it is essential that the colouring-matter should be thrown down on or together with some suitable medium.

The manufacture of lake pigments may be likened to dyeing, for the dyer has to produce a given shade on cloth or yarn, while the lake-maker has to produce a given shade on some base or bases, and his lot is the harder, inasmuch as the bases, as a general rule, have no affinity for the colouring-matter of which he can take advantage. In many cases, also, it is essential that the base possess certain definite properties, if the finished lake is to be suitable for the purpose for which it is designed; and, in matching a pigment, not only has the shade and strength to be correct, but the base must also be matched, if the product is to be satisfactory in every way. Though the lake-maker escapes the complications of the dyes arising from the variation of similar fibres from different sources, the chemical and physical nature of the base or matrix on which the lakes are developed, whether it be a simple inert body or a complex mixture obtained by precipitation,
needs as much if not more consideration and study than the actual production of the lake itself. Considerable experience in the production of lake pigments on a commercial scale renders it a moot point whether the conversion of the colouring-matter into an insoluble pigment, or the adjustment of the bases to suit the requirements of the various uses of the pigments, is the key to their successful and economical manufacture.

It would be advisable, perhaps, at this stage to consider the exact function of the base in a lake pigment. We have seen in Chapter I. that a lake is usually understood to be a dyestuff converted into an insoluble coloured compound; but, in the majority of cases, this compound does not become a workable pigment, until it is combined with some other body or bodies giving to it those physical properties without which its practical application would be impossible.

There is a considerable difference between the base of a lake, and the filler or extender that is used in the paint trade to let down strong colours. A lake containing 10 per cent. of eosine on barytes is definitely understood to mean a pigment containing 10 per cent. of eosine lake struck on 90 per cent. barytes; but a 20 per cent. eosine lake on barytes, let down with barytes until it contained 10 per cent. of colouring-matter, cannot properly be called a 10 per cent. eosine lake pigment, though if the mixture were well made there would be very little difference between the two products. The struck 10 per cent. eosine lake pigment would be the better article, since the lake would be more evenly and intimately spread over the whole of the barytes, but, in preparation, there would be greater bulk to handle and dry, with consequent increased labour and expense. It behoves the manufacturer of lake
pigments to determine, when considering cases, of which this is but a very simple example, the most economical quantity of base it is desirable to use. This question becomes a very serious one in the production of such pigments as those produced from Lithol Red R and other pigment colours, and will be more fully discussed when dealing with the production of pigments from this class of colouring-matters.

There are some lakes, of which the alizarine lakes are typical, which may be looked upon as lakes pure and simple, capable of being used without the addition of anything that may be called a base. For the development of the colouring-matter, the latter must be treated with aluminium, calcium, stearine, and certain other colourless bodies which, by direct combination with the alizarine, give rise to a coloured compound, known as the lake. The shade and intensity of the lake produced depends not only on the nature of the colouring-matter, but on its state of combination in the finished product. The shade and strength of these lakes, however, may be varied by the amount of colouring-matter used, and, therefore, the complex mixture of acid salts which are capable of developing the colour of alizarines must be looked upon as the base in these pigments.

Basic colours, which are absorbed by white and green earth, and form fairly stable combinations, e.g., malachite green, can be regarded in somewhat the same way. The earths referred to consist mainly of siliceous matter naturally impregnated with compounds of organic origin which combine with the dyestuffs, the shade and strength of the pigment produced being determined by the amount of colour that is absorbed or enters into combination. The green earth is also a determining factor in the nature of
the resulting product in so far as it has not an unlimited capacity for absorbing colouring-matters, this property being governed by its quality, which again depends on its source and mode of preparation for use.

It is perhaps therefore advisable to divide the bases used for lake pigments into three divisions:—

(a) Those in which the base acts merely as an extender and has no chemical relationship with the colour lake.

(b) Those in which the base and the lake are in definite chemical combination.

(c) Those having the combined properties of (a) and (b).

There can be defined, however, no sharp line of demarcation where a base ceases to be a base and becomes a filler or extender. Especially is this true in the case of pigment colours on barytes or other similar base, where anything from 2 per cent. to 50 per cent. of colouring-matter may be required; but terra-alba and china clay present in an alizarine lake and green earth colour respectively, could not be regarded as anything but diluents.

The following is a list of the substances usually composing the majority of bases. Most are insoluble in water, and are either used in the form mentioned, or are produced at the same time as the lake, or during some operation in the production of the pigment:—

I. Barium sulphate, as barytes (natural) and blanc-fixe (precipitated), $\text{BaSO}_4$.

II. Clay.—China clay, a compound silicate of aluminium.

III. Calcium sulphate.—Paris white, gypsum (natural). satin white (precipitated), $\text{CaSO}_4$.

IV. Kieselguhr.

V. Red lead.

VI. Zinc oxide.
VII. Lead sulphate, PbSO₄.
VIII. Aluminium hydrate, Al₂(OH)₆.
IX. Phosphate of aluminium, AlPO₄.
X. Aluminium arsenite.
XI. Phosphate of barium, Ba₃(PO₄)₂.
XII. Phosphate of calcium, Ca₃(PO₄)₂.
XIII. Lamp and vegetable black (carbon).
XIV. Green and white earth.
XV. Lead carbonate, white lead.
XVI. Calcium carbonate, chalk.
XVII. Lithophone.
XVIII. Orange lead.

These compounds are introduced into the pigment by grinding, as in the case of the pigment colours, by suspension in the solution from which the lake is precipitated, by formation from suitable reagents at the time of precipitation of the lake, or by a combination of the two latter methods, e.g., when using mixed bases, suspending one in water and producing the other simultaneously with the lake.

Barium sulphate occurs naturally as heavy spar, and, when ground, comes into the market under the name of barytes. According to the traces of metals it contains, it is coloured grey or brown; but for all classes of pigment-making only the pure white, very finely ground product should be used. It possesses but little covering power in oil, and, when used for the preparation of pigments for oil-work, it is advisable to mix with it lead sulphate in the case of cheap goods, or lead carbonate and red lead (when shade allows) for those of better quality. For some classes of pulp colours, barytes is extremely valuable, since, compared with other bases, it gives very bright and full shades with small amounts of colouring-matter.

The precipitated variety is obtained by precipitating
the sulphate from a soluble barium salt, by means of sulphuric acid. The fineness of the particles, on which the quality greatly depends, is varied according to the method of precipitation. This product is now available in the market in fairly large quantities both in pulp and dry, but, where uniformity of quality is desired, it is always advisable for the lake manufacturer to prepare it himself. To secure uniformity, the essential requirements are: both the solution of the soluble barium salts and that of the sulphate, whether it be sulphuric acid or a soluble sulphate, must be always of the same concentration; the stirring of the mixture, the method of addition, and, above all, the temperature at which the blanc-fixe is struck must not vary. Sulphuric acid may be used, but it is preferable to use a soluble sulphate: Glauber's salt or sodium sulphate is the one generally selected, because it is cheap. The sulphate should be added just slightly in excess, in order that the whole of the barium may be thrown down. Witherite, native barium carbonate, can be used as the source of the barium salt. Dissolved in hydrochloric acid, in the presence of an excess of the mineral, a solution of barium chloride is obtained fairly free from iron, since the witherite, when in excess, causes the reprecipitation of any dissolved iron compounds.

The precipitated barium sulphate settles very readily, and must be washed free from acid, if acid has been used in its production. In many cases the product is too fine to filter-press economically, but this difficulty is readily overcome by the addition of a little ammonia neutralized sulphonated castor oil, about 0.1 per cent. of the weight of BaSO\textsubscript{4} to be separated; this causes the particles of the blanc-fixe to become floculent, allowing the whole to be readily filter-pressed, and in no way injuring the properties
or nature of the material to which it has been added. Precipitated barium sulphate is known commercially as blanc-fixe, permanent white, and enamel white, and is largely used as a base for pulp colours, since it gives a fine solid appearance, and, above all, works out on paper perfectly smoothly, differing in this respect from barytes, which, however finely ground, imparts a rough feeling to any pigment that it contains, rendering it an unsuitable base for pulp colours for surface papers. There is a great difference in the shade produced when equal weights of colour are precipitated in the same way on equal weights of barytes and blanc-fixe, the shade on barytes being much fuller and brighter than that on blanc-fixe, which is, in addition, frequently of a different tone.

Pulp colours made purely from either of these varieties of barium sulphate retain but little water, and soon become hard and dry.

China clay, or kaolin, a naturally occurring substance, is a hydrated silicate of aluminium, derived from the clay of felspathic rocks, and, when of good quality, contains only traces of impurities, in the form of oxides of iron, calcium, and magnesium. It forms an extremely valuable base for lakes, especially in combination with other bodies; and is capable of retaining about 60 per cent. of water, giving pulps of a smooth appearance and finish. Like barium sulphate, it has no chemical affinity for dyes, though it is often coloured by being saturated with solutions of colouring-matters, which, however, can be entirely removed by washing. Lakes in which a large proportion of clay has been used are apt to have a "chalky" and "bright" appearance, which detracts very considerably from their value, and rather dulls the shade; also in the final washings the clay has a tendency to hang, taking a very con-
siderable time to settle. In combination with hydrate of aluminium these objectionable qualities largely disappear. Such combinations can be more readily discussed when dealing with other similar aluminium hydrate mixtures.

China clay, whose density is much less than that of either gypsum or barytes, is used mixed with these bodies, to give lightness and to diminish their coarseness. With some lakes, more especially the pulp lead eosine lakes, the use of china clay in conjunction with blanc-fixe makes the pulp less tenacious, and lighter, and, by causing the lake to retain more moisture, improves the keeping qualities and yield.

Calcium sulphate, gypsum, Paris white, occurs naturally as satin spar, gypsum, alabaster, etc. The whole of the water of the naturally occurring body $\text{CaSO}_4 + 2\text{H}_2\text{O}$ is driven off between $110^\circ$ to $120^\circ$ C., the residue being known as burnt gypsum or plaster of Paris, which can be readily identified by its property of combining with water, with evolution of heat and subsequent solidification. When heated above $200^\circ$ C. gypsum becomes "dead burnt," and then only takes up water slowly, without hardening.

Calcium sulphate is distinctly soluble in water, much more so in the presence of ammoniacal salts—especially of acetates. It is readily soluble in strong hydrochloric acid, and this solubility sometimes causes it to be overlooked in the cursory examination of lakes.

Owing to its solubility, it is not a suitable agent for use in the preparation of lakes by precipitation.

A mixture of calcium sulphate and aluminium hydrate, known as satin white, made by adding potash alum to milk of lime and stirring the mixture until the reaction is complete, is largely used in the surface and wall paper trade for producing fine smooth finishes. It is alkaline in its
reaction, and care must be taken with colours, especially reds, used in conjunction with this material, that they are so prepared as to prevent bleeding when mixed with it in size.

Terra-alba is largely used in the manufacture and reduction of dry pigment colours, since it is much lighter, and of greater covering power, than barytes.

Red lead, or minium, \( \text{Pb}_3\text{O}_4 \), litharge, \( \text{PbO} \), and orange lead, red lead free from litharge, are chiefly used, in producing shades of vermillionettes and permanent reds, in conjunction with other bases, such as barytes, lead sulphate, and lead carbonate, and other lakes which are used as paints, in order to modify the shade and improve the body and covering power.

Orange lead is the only oxide of lead which should be used in the preparation of lakes; the other oxides act very powerfully on linseed oil, and, when used to reduce the price of the pigment, render it of no value whatever for use with oil as a paint.

Lead sulphate, \( \text{PbSO}_4 \), is used mainly as a base instead of barytes, for intermediate classes of colours. For paints where the price prohibits the use of white lead, or where the reactions involved in the formation of the lake would decompose the carbonate, a cheap useful sulphate of lead, known as "lead bottoms," can be obtained. This is a by-product obtainable from calico print-works and paper-works, and being a precipitated sulphate is very fine, and gives excellent results. It contains some impurities, and requires thorough washing before use as a lake base.

White lead, or lead carbonate, is used only for paint colours; its well-known physical and chemical properties do not call for treatment here.

Zinc white, \( \text{ZnO} \), is rarely used alone as a lake base, though, like the lead compounds, it finds application
occasionally in the manufacture of oil colours. It is, however, of great use in the production of azure blues from the Erioglaucines and Patent Blues of L, M, and B, since for some reason, when present in small quantities in the base used, the colour is more completely thrown down. The explanation of this cannot be satisfactorily given, but nevertheless the presence of from 2 to 6 per cent. saves considerable colour.

Lithophone, a mixture of precipitated barium sulphate and zinc sulphide, containing in good qualities about 30 per cent. of zinc sulphide, is not used in the precipitation process, as the slightest acidity would lead to the decomposition of the zinc sulphide; but, in dry grinding of such pigments as Helio Fast Red R. L., where greater body and covering power are needed than blanc-fixe gives, it is used to a fairly considerable extent.

Lamp, vegetable, and allied blacks are used as bases for deep shades of olive-green and blue, being first made into a paste or thin cream with water—easily effected if the operation is started with a little glue and ammonia, and water added until the proper consistency is obtained—and then the required colours added and precipitated with or without the addition of any other base.

Chalk, or calcium carbonate, CaCO₃, which occurs native as limestone, chalkstone, marble, etc., and in its artificial form as precipitated chalk, is but little used in the manufacture of pigments, owing to its sensitiveness to the action of the weakest acids; but it is of great service when employed in small quantities to eliminate traces of acid. If used in large quantities, owing to its solubility in water containing carbon dioxide, it gives a milky appearance to the pulp colours when worked with size, and the other bases give more pleasing effects without many of the drawbacks that
this body has, such as frothing when worked with size. For paint colours these objections do not so much apply as for pulp, but chalk is not a base to be recommended.

Kieselguhr, a finely divided infusorial siliceous earth, largely used in the manufacture of dynamite, is used with the heavier bases to make the lake lighter. It finds its widest application in pulp colours where such bases as barytes and blanc-fixe are used, since the latter retain but little moisture, while kieselguhr possesses the property of retaining a large amount of water without becoming too thin and pulpy, rendering the pigment more easily worked in size, etc., besides increasing the body and density of the colour.

Green earth.—This is a similar substance to kieselguhr, and has the property of taking up, and being dyed by, basic colours, notably greens and blues, giving highly coloured bodies of much superior fastness in every respect to the lakes produced by the ordinary methods. They are fast to weak alkalies and have a great vogue in distemper work. Analysis of the earth shows it to be a mixture of hydrated oxide of iron, silica, and calcium compounds, together with a variable amount of nitrogenous organic matter of an acid nature. Varieties of green and white earth differ very considerably in their capacity for taking up colours and forming satisfactory lakes, this variation being dependent on the manner in which they are prepared for market and the nature and amount of organic matter they contain.

Apart from its colour white earth is very similar to green earth and possesses the same properties, but does not give quite such satisfactory, though brighter, results.

The presence of hydrated oxide of iron in these two earths may in some measure account for the properties of the earth, for in the presence of the organic matter it may have all the action of a strong iron mordant.
PLATE II

 Manufacture of Lake Pigments

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On Plate II are shown a series of shades given by basic dyestuffs on Green Earth:

No. 1 shows 2 % Auramine O (Brit. Dyes) on Green Earth.
No. 2 " " Chrysoidine YRP " " "
No. 3 " " Bismarck Brown " " "
No. 4 " " Methylene Blue 2 B " " "
No. 5 " " Methyl Violet " " "
No. 6 " " Magenta Crystals " " "

In Plate IIa (Frontispiece) are shown a series of shades given by basic dyestuffs on White Earth:

No. 1 shows 1 % Auramine O (Brit. Dyes) on White Earth.
No. 2 " " Chrysoidine YRP " " "
No. 3 " (0.6 %) Malachite Green Crys. " " "
No. 4 " (0.4 %) Auramine O " " "
No. 5 " 2 % Methylene Blue 2 B " " "
No. 6 " 1 % Methyl Violet " " "
No. 6 " " Magenta Crystals " " "

Aluminium hydrate, Al₂(OH)₆, is rarely used other than freshly prepared, and the preparation is usually effected by precipitation from the solution of a soluble salt, usually sulphate of aluminium, with sodium hydrate or carbonate, the carbonate being generally employed. The reaction which takes place can be expressed as follows:

\[
\begin{align*}
\text{Al}_2\text{(SO}_4\text{)}_3 + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} &= \text{Al}_2\text{(SO}_4\text{)}_2\text{(OH)}_2 + \text{Na}_2\text{SO}_4 + \text{CO}_2 \\
\text{Al}_2\text{(SO}_4\text{)}_2\text{(OH)}_2 + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} &= \text{Al}_2\text{SO}_4(\text{OH})_4 + \text{Na}_2\text{SO}_4 + \text{CO}_2 \\
\text{Al}_2\text{(SO}_4\text{)}_4(\text{OH})_4 + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} &= \text{Al}_2(\text{OH})_6 + \text{Na}_2\text{SO}_4 + \text{CO}_2
\end{align*}
\]

The formation of the basic sulphates takes place more readily in cold dilute solution, and, of them, notice need only be taken when dealing with cold dilute precipitations, where their formation, in the absence of enough alkali, may lead to a loss of weight, owing to their solubility. The basic compounds, are, however, decomposed by heat.

Sodium hydrate is very rarely used to effect this precipitation, since aluminium hydrate acts like a weak acid with strong bases forming aluminate, and in consequence is easily soluble in an excess of this reagent.
On the proper preparation of the alumina the production of the best results depends, for, if the solutions used be too strong, the alumina is imperfectly precipitated, and the finished lake permeated with numerous white specks. If an excess of alkali is used, a greater proportion of barium chloride has to be employed, with consequent weakening of the shade, and the resultant pigment often bleeds. If the solutions be too dilute and cold the precipitation is frequently only partial, and the lake has a tendency to "hang," i.e., not to settle in the subsequent washing operations.

Potash alum, owing to its greater cost and greater insolubility in water, is used only in the manufacture of those lakes which are required to have a fine fracture, in order to obviate the danger arising from too strong solutions; but aluminium sulphate can be used just as well, if care on the points of dilution and temperature be observed, for the strength of solution which would give good results with an ordinary pigment would, owing to the greater flocculency of the particles, be unsatisfactory in the case of a lake required to show a clean fracture.

Pigments containing a large proportion of alumina often tend to dry very hard and are difficult to work. This difficulty can frequently be overcome, without deteriorating the quality of the lake, by the addition of from 5 per cent. to 20 per cent. of disodium hydrogen phosphate which is precipitated as aluminium phosphate in the course of the reactions, and does not impair the transparency of the lake in oil or ink but softens the texture and makes it much easier to work.

Aluminium hydrate is used pretty largely for certain classes of colours which can hardly be termed true lakes. Since the colouring-matter is but partially fixed by the aluminium hydrate, there is always a large loss of colour,
but in the case of such products as confectionery colours, where the use of other precipitating agents is not permissible for obvious reasons, this property of aluminium hydrate of partially fixing colouring-matters is largely utilized.

It is chiefly used in conjunction with other bases, because it adds brilliancy and fastness to the pigment, by combining with the hydroxy groups; and for pulp colours, because it renders the colours easier to work, removing their stiffness and hardness, and, owing to its gelatinous nature, retains much water. Alone, aluminium hydrate does not give a pigment of much value, since the product is lacking in body and opacity.

The method used for the preparation of the mixtures of aluminium hydrate and other bases is to suspend a base like China clay in a solution of aluminium sulphate, and, while vigorously agitating the mixture, to add slowly the sodium carbonate.

The temperature and concentration of the solutions when mixed depend mainly on the consistency and properties required of the base; and it may be taken as a general rule that, where small quantities of the hydrate are about to be produced, it is not so much that the aluminium hydrate is desired to influence the nature of the base, as to assist in the fixation of the colour. It is advisable, therefore, to use the solutions fairly dilute and not above 45° C. Where proportionally large quantities of aluminium hydrate will be produced, it is advisable to use rather more concentrated solutions and to precipitate at the boil; otherwise there appears a lack of body in pulp colours, and the dry colours are extremely hard, the quantity of aluminium hydrate making amends for the diminished attraction it has for the colouring-matters.
The following proportions have been found serviceable as bases for reds, oranges, and greens:—

For oil colours.—(1) 448 barytes, or lead sulphate.  
" 25 aluminium sulphate, 17 per cent.  
" 8:75 sodium carbonate, 58 per cent.,  
45° C.  
" (2) 560 blanc-fixe.  
" 25 aluminium sulphate, 17 per cent.  
" 8:75 soda ash, 58 per cent.

For pulp colours.—112 China clay, blanc-fixe, or barytes.  
" 100 aluminium sulphate, 17 per cent.  
" 35 soda ash, 58 per cent.

The aluminium salts of the polybasic acids, such as phosphoric and arsenious acids, are largely used in the preparation of the lake and base simultaneously, especially with strongly basic colours, e.g., magenta, with which these acids seem to combine readily to form lakes. The two aluminium salts most usually employed for this purpose are the arsenite and phosphate.

The arsenite is prepared by dissolving white arsenic, arsenious oxide, As₂O₃, in a fairly concentrated solution of sodium carbonate, by boiling for at least half an hour: the solution is then diluted and run into a solution of aluminium sulphate containing the colouring-matter and a little sodium acetate. The sodium acetate is used because free acetic acid and acid acetates have much less action on the base and lake than mineral acids and their acid salts. If the precipitation be effected in an acid solution, the resultant lake dries very hard and dark, losing all its brilliancy and bloom; it is very difficult to wash properly, and is of so slimy a nature that it is extremely difficult to handle. The nature of the precipitate, when formed in the presence of an excess of alkali, is entirely different,
being quite free from sliminess, and of good body and covering power, but, unfortunately, it bleaches many of the colours, and with others it prevents precipitation. It is, therefore, essential to arrange that the mother liquor of the mixture should have an almost neutral or only slightly acid reaction, since, if it be but slightly alkaline, in some cases, after the colour is used and exposed to air, it deepens, ruining the shade. The presence of a small quantity of sodium acetate, itself a salt with an alkaline reaction, partially neutralizes the acid effect of a very slight excess of aluminium sulphate, and produces a better and more pleasing result.

It may be pointed out that when a solution of sodium acetate is mixed with a solution of aluminium sulphate, partial mutual decomposition takes place, with the formation of sodium sulphate and aluminium acetate; and on the addition of the alkaline solution there are reasons to believe that the sulphuric acid of aluminium sulphate, having a stronger affinity for the alkali than the comparatively weak acetic acid of the acetate, is primarily acted upon, so that the acid aluminium salt in excess, in all probability, is mainly acetate, which has, as previously pointed out, a much more feeble action on the precipitate.

Phosphoric acid, as pointed out in a previous chapter, is especially adapted for the precipitation of the violet basic colours, and certainly the violet lakes yielded by it are very bright, particularly when they are produced on a base of phosphate of aluminium.

The most usual method of procedure is to mix the solutions of the colour or colours with a solution of aluminium sulphate, and then to run in a solution of sodium hydrogen phosphate, to which has been added sufficient carbonate of soda to produce, on mixing with the aluminium
solution, a perfectly neutral precipitate, in accordance with the following equation:

$$\text{Al}_2(\text{SO}_4)_3 + 2\text{Na}_2\text{HPO}_4 + \text{Na}_2\text{CO}_3 = \text{Al}_2(\text{PO}_4)_2 + 3\text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{CO}_2$$

If the solution be either acid or alkaline, there is sure to be loss, for, in the first case, the pigment will be very gelatinous and slimy, and, in the other, the colour will not be by any means completely thrown down. This precipitation is best conducted with 10 per cent. solutions at the boil; if stronger solutions be used, the pigment is contaminated with small white lumps, and, if the solutions be too weak or too cold, the lake has no body, and retains far too much moisture, besides being difficult to handle.

The phosphates and arsenites of aluminium have the property of combining with the basic colouring-matters, after they have been precipitated. Some makers find that they get better results by first of all carefully preparing the required salt of alumina, washing it as free as possible from all soluble salts, adding the solution of whatever dye-stuff is being used acidified with acetic acid, and gently raising the temperature, when the colour combines readily with the base giving the required result. Either method is satisfactory and gives equally good results. The method adopted is better determined by the experience of the operator. In both these methods the addition of a little turkey-red oil in very dilute solution after striking, improves the nature of the lake, but it should not be more than about 2 per cent. of the amount of dry lake which the batch is expected to yield.

Phosphates of barium, calcium, and lead are also precipitated along with the lake in some instances; but they are not very largely used, and are only of use when match-
ing a particular shade, since the lakes produced by other
means are usually superior to them.

Barium sulphate is very often precipitated together
with the lake, but this is usually done when mixed bases
are being used, and when both methods are being used to
introduce the base into the pigment. It avoids the use of
too much or rather too great a mass of inert matter which
is not always easily kept in suspension, especially when
the substance is a heavy one like barium sulphate, and
brings about a more intimate mixture of the whole base
than could otherwise be effected by mechanical means.
The following example will illustrate the general method
adopted:—

1. A clay, blanc-fixe, and aluminium hydrate base—
   56 parts of China clay, suspended in a solution of
   100 ,, of aluminium sulphate, 17 per cent., treated
   with a solution of
   35 ,, of sodium carbonate, well stirred, the colours
   added, and the requisite amount of barium
   chloride run in, say,
   100 ,, of barium chloride.

By the addition of the sodium carbonate to the alu-
minium sulphate solution containing the clay, the alu-
minium hydrate formed is more thoroughly incorporated
with it than it would be by any merely mechanical admix-
ture. On the addition of the barium salt, the barium
lake is formed, and, at the same time, the excess of barium
combines with the sodium sulphate formed on the de-
composition of the aluminium sulphate, giving barium
sulphate, or blanc-fixe.

This example illustrates very well the reason why
pigments produced by this and similar methods are clearer
and brighter than those simply precipitated on inert bases; for, however well the mixture may be agitated during precipitation, in such cases the pigment consists of the inert base fully or partially coated with the lake and free lake particles. In such a method as described above, the China clay is practically coated with the gelatinous precipitate of aluminium hydrate, which retains a considerable amount of the sodium sulphate, and often, on the addition of the colour, partially combines with it as well as exerting its natural property of absorption; therefore, when the barium chloride is added to the mixture, the formation of the lake and of barium sulphate takes place in the particles of the suspended colouring-matter as well as in the thoroughly incorporated mixture produced by the reaction of the colour, barium chloride, and sodium sulphate.

In Plate III are shown a series of shades produced by acid dyestuffs by barium chloride on the clay or blanche and alumine base:

No. 1 shows Acid Yellow 79210 (Brit. Dyes).
No. 2 " Metanit Yellow " " "
No. 3 " Citronine R " " "
No. 4 " Orange WH " " "
No. 5 " Scarlet R " " "
No. 6 " Scarlet 3 R " " "

Examples of these mixed methods might be shown for each class of colouring-matters, and yet none be given to meet some special and individual case. It is by far the best plan for each colour-maker to examine carefully the colour, and to devise for himself the most rational way of producing the best result; and, by adopting those bases which he knows from experience to be most suitable for the purpose for which the pigment is required, to experiment
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until he arrives at the most satisfactory result. What works well in one man's hands in a certain place does not, owing to differences of method and appliances, work well with another man in another place, and it is as well to work out personally those methods most suitable to the conditions under which the maker labours.

In conjunction with the use of aluminium hydrate bases, especially with colours that give better results when the solution of the dyestuff is added in slightly acid solution, improvement in the texture and nature of the base have been obtained by using phosphoric acid in place of acetic.

The pure ortho-variety is now easily obtained, of a specific gravity varying from 1250° to 1750°, the weaker strength being the cheaper. It can be obtained free from even traces of iron, is not a dangerous acid to use, and, in conjunction with colouring-matters containing amido, hydroxy, and sulphonic-acid groups, has a tendency as phosphate of aluminium to brighten the shade and improve its fastness generally.
CHAPTER VII.

THE PRINCIPLES OF LAKE FORMATION.

An examination of the constitution of the artificial colours and the methods adopted to form lake pigments from them shows that the latter is effected by combining the colours with metallic or various acid bodies, both organic and inorganic; in other words, the formation of salts, in which the colouring-matter plays the part of the acid or base.

In order, therefore, to consider the general principles to be followed in the production of lake pigments from artificial colours, it is necessary to divide them into four classes—

I. Purely basic colours.
II. Purely acid colours.
III. Compound colours of both an acid and basic nature.
IV. Azo colours.

The basic colours are those containing amidoo or substituted ammonia groups, either simply, or in such positions and preponderance over weak acid groups that the acid functions of such groups may generally be regarded as negligible from a lake-forming point of view.

The acid colours include a much larger number of lake-forming groups, namely, the hydroxy, nitro, carboxyl, and sulphonic-acid groups—one or more of which may occur in the same colour molecule, together with a lake-forming group of a basic nature.

It is necessary to consider carefully the method of
procedure to be followed where the lake-forming group or groups in a colouring-matter are of a simple nature, capable of forming simple lakes readily, and where the colouring-matters are of a more complex constitution, containing several groups, giving satisfactory results only when compound lakes are formed from them, though they are often capable of being thrown down by the action of some reagent on one or more similar groups.

The production of lakes from artificial colours cannot be regarded as the mere precipitation of a colouring-matter on a base to form a lake, for almost all colouring-matters are insoluble in strong solutions of common salt, yet the precipitation of such a colour by common salt on an inert base produces but a mechanical mixture of the colour and the base from which the colour can be redissolved unchanged. A lake pigment must be regarded as a chemical combination of the dyestuff with one or more bodies, conferring on it pigmentary qualities, and in most cases giving a body of the type of the original colour, but of a different chemical composition. Whether these combinations are of the nature of simple exchanges, the reactions being capable of expression by simple chemical equations, is a very debatable point. In some cases experimental data indicate such simple changes, but in others the present knowledge of the actual constitution of the pigment is a very open question.

When a solution of a dyestuff, more particularly the basic colours, is added to starch, clay, etc., a certain amount of colouring-matter is taken up. This cannot be accounted for by any chemical attraction of these various bodies for the colouring-matter, but it may be due to partial dissociation of the colouring-matter producing the free colour acid or base, which is attracted to and adheres
to the particles of the insoluble matter present in the mixture. This is most evident in the case of weak bases combined with weak acids. Though the cause of this seeming absorption cannot be clearly elucidated, there can be no doubt that the colouring-matter in such a pigment cannot be looked upon as a true lake, but simply as an intimate mixture of insoluble matter and uncombined colouring-matter; and the extremely fugitive properties of such coloured bodies to air and light, as well as their want of fulness and brightness, confirms this idea, prompting one to condemn entirely such methods of producing colours and styling them lakes.

This apparent absorption of colouring-matter may also be the property of a true lake: for many colours, especially those of a basic nature, often require but a tithe of the precipitating agent to entirely precipitate them that an examination of their formula would lead one to think would be required. For instance, a molecule of magenta requires theoretically a molecule of tannic acid, but it can be almost entirely precipitated by about a third of that quantity. It is scarcely conceivable that the addition of tannic acid leads to a rapid dissociation of the magenta molecule, though perhaps the tannic acid and magenta compound may possess considerable attraction for the free colour base; but the compound produced by tannic acid, which is trihydroxy acid, may possess the property of taking up or being dyed by the uncombined soluble salt of magenta, and thus cause the seeming absorption of the rest of the colour. Where the full amount of tannic acid is used, the lakes are more permanent, but not so bright as those in which only the minimum quantity has been employed. The plan of using but the necessary quantity of tannic acid in these cases to secure greater brightness has obtained for
the tannic acid lakes a reputation for being far more fugitive than they really are, and has resulted in their being ranked but little faster than the fugitive lakes produced by such acids as arsenious and phosphoric. In point of fact they are the most permanent of all the lakes produced from basic colours.

Where a colouring-matter contains several lake-forming groups, which are capable of entering into combinations with various reagents, the full value of the chromogenic power and the most satisfactory and permanent results are obtained when as many as possible of such groups are combined with those bodies for which they have an affinity.

A very good example of this can easily be demonstrated by a colour such as concentrated Acid Green D (M. L. & B.), which yields fairly fast green lakes by precipitation on aluminium hydrate with barium chloride. The precipitation is almost complete, but an appreciable amount of colour remains in solution; or, more correctly expressed, the simple barium lake is soluble in water, giving the impression that the whole of the colouring-matter is not thrown down. If, previous to the addition of the barium chloride, tannic acid be added to the solution of the colouring-matter the precipitation is complete, and a much faster, brighter, and more insoluble product is obtained. The improvement in the properties of the lake by this addition is not due to any action of the tannic acid per se: but, as the colour, Acid Green D (Conc.) is an amido-sulphonic acid, the amido or basic properties are in the first place satisfied by combination with the tannic acid. The latter reagent has not the power alone to form a lake from such a strongly acid colour, therefore no precipitation or very little occurs until the addition of the barium chloride, which, combining with the sulphonic acids, throws down the barium
tannic acid lake of the colour in which the affinity of the various lake-forming groups has been completely satisfied, giving in consequence a more stable body, and developing to a much greater extent the colouring power of the dye-stuff.

It does not follow because a colouring-matter contains lake-forming groups that it is capable of being converted into a pigment, for the properties of the ordinary combination which precipitates a similar colour may differ, just as the chloride of silver is insoluble and the chloride of sodium extremely soluble; or the groups themselves may be so arranged in the colour molecule, and be so opposite in character, though capable of being used for application to textile fibres, that they cannot by any means, simple or compound, be precipitated satisfactorily as a lake pigment. A good example of such a colour is acid magenta, a triamido-sulphonic acid.

The formation of lakes from basic colours is dependent on the combination of the amido or basic group or groups in the colour molecule with various acids, producing insoluble salts of the colouring-matters.

In the majority of cases the lake is produced together with the whole or part of the base, ensuring the presence of an excess of the precipitating body since the reaction is brought about by precipitating the insoluble metallic salt, together with the insoluble salt of the colouring-matter. Such methods may be regarded as the precipitation of an ordinary mixture. But, as has already been remarked, the lakes produced in this way from phosphoric, arsenious, palmatic, resinic acid, etc., though very bright, are very fugitive, and often extremely poisonous. Their manufacture is a matter of great simplicity when due care is paid to the chemical properties of the various compounds used in their production.
The most permanent lakes produced from basic colours are the tannic acid lakes, which, though duller even when correctly prepared, are much more permanent than the lakes produced from these colours by other means. A magenta salt, e.g., the hydrochloride, gives a tannic acid lake as follows:

\[
\begin{align*}
\text{C}_6\text{H}_4\text{NH}_2 \quad \text{when converted into} \\
\text{C}_6\text{H}_4\text{NH}_2\text{HCl} \\
\text{the tannate gives} \quad \text{C}_6\text{H}_4\text{NH}_2 \quad \text{C}_6\text{H}_2(\text{OH})_3\text{COO} \\
\text{C}_6\text{H}_4\text{NHCOO} \quad \text{(HO)_2H}_2\text{C}_6
\end{align*}
\]

This salt is soluble in the hydrochloric acid liberated, and although almost complete precipitation is obtained if an excess of acetate of soda be added before the tannic acid, or by using tannate of soda, such lakes are very dull, and their permanency but little better than the lakes of other acid bodies. The full value of tannic acid is only shown when it is used in conjunction with a salt of antimony, preferably tartar emetic, which, as it is a tartrate, is able of itself to combine with the basic colouring-matter, although in but few instances are the precipitates insoluble in hot water. When tannic acid is added to the mixture in presence of sodium acetate, the whole of the colour is precipitated as a double antimony and tannic acid lake. The latter, though not as bright as the arsenuous acid lakes, is much brighter and far more permanent than those produced from tannic acid or tannate of soda.

The determination of the exact amount of tannic acid to be used with each individual colour is a matter of considerable difficulty, for it has been shown that, though in many cases the amount of tannic acid theoretically
required for a pure colour is more than sufficient to precipitate the colouring-matter, whether it be all thrown down as a lake is a matter of considerable doubt, increased by its physical behaviour. Where the theoretical amount is used, a much faster, though, at the same time, duller lake is produced. No reliable data can be obtained by simply titrating solutions of the dyes with tannic acid. If an excess of tannic acid be used, it greatly interferes with the working of the colour, besides increasing the cost to no purpose, but where the constitution and the purity of the colour employed are approximately known, it is by far the wisest plan to use the theoretical amount. Hence it is very important in making lakes from basic colours to use those brands which are commercially pure, and whose chemical nature and constitution are known.

Various researches have shown that a molecule of tannic acid is fixed by about half a molecule of tartar emetic, though from an examination of the two bodies it would have been surmised that a molecule of tannic acid would have required a molecule of tartar emetic. This is borne out in practice, since if, previous to the addition of tannic acid, this proportion of tartar emetic be added to the mixture, complete precipitation takes place; and in cases where the exact constitution of the colouring-matter cannot be ascertained, and an excess of tannic acid is used, it is advisable to maintain this proportion, so that the injurious effects produced by an excess of these reagents is reduced to a minimum. The tannic acid and tartar emetic not required to combine with the colour are precipitated as a compound salt of antimony. Therefore, in producing lakes from basic colours, wherever possible tartar emetic and tannic acid should be used, and, in order to obtain the best results, the molecular ratios between the colouring-
PLATE IV

Manufacture of Lake Pigments

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matter and the two lake-forming bodies should be maintained.

The conclusion to be drawn, therefore, is that for tannic acid lakes it is advisable not to precipitate them simply as tannates of soda, but to combine them with some double salt of tannic acid, such as that formed by the combination of tannic acid and tartar emetic. For special shades and tones the tannic acid compounds of iron and tin are of great service, but on account of the reducing action of stannous chloride great care must be exercised in using this reagent.

Plate IV shows a series of shades produced by means of Tartar Emetic and Tannic Acid by basic dyestuffs:—

<table>
<thead>
<tr>
<th>No. 1 shows Auramine (Brit. Dyes).</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 2 &quot; &quot; Auramine Malachite Green Crystals &quot; &quot; &quot;</td>
</tr>
<tr>
<td>No. 3 &quot; &quot; Malachite Green Crystals &quot; &quot;</td>
</tr>
<tr>
<td>No. 4 &quot; &quot; Methylene Blue 2 B &quot; &quot;</td>
</tr>
<tr>
<td>No. 5 &quot; &quot; Methyl Violet 2 B &quot; &quot;</td>
</tr>
<tr>
<td>No. 6 &quot; &quot; Magenta Crystals &quot; &quot;</td>
</tr>
</tbody>
</table>

The lake-forming groups in the acid colouring-matters are more numerous, and require various methods for their precipitation.

The property that basic and acid colouring-matters have of combining with each other is utilized in tinting colours to various shades. Though perhaps the result of such combinations leads to the ready production of the required shade, such means should only be used with great discrimination, for such combinations often readily dissociate, and give by no means permanent pigments. It is far better, where practicable, to combine each colour with its typical lake-forming compound.
The property of purely amido salts of combining with amido-sulphonic acids has been made use of in the production of pure lakes from such colours as Alkali Blue and Victoria Blue, having a strong staining colour with a high bronze suitable for replacing Chinese Blues in the manufacture of lithographic inks. The method of procedure will be dealt with in the chapter dealing with blue lakes.

Of the acid colours, the nitro derivatives are perhaps least used, because their metallic salts are usually extremely soluble. The few combinations with the oxides of the heavier metals are not of such a nature as to be esteemed as pigments.

The hydroxy group is a powerful lake-forming group, which occurs in those colours from which the fastest, most permanent lakes are produced, yet its value as a lake-forming group is not great in the monohydroxy compounds, but only in those where it occurs as a dihydroxy derivative.

The position of the hydroxy groups in the molecule exerts considerable influence on the lake-forming properties, for, unless the hydroxy groups be in the ortho-position in respect to each other, the lakes produced are not fast, but may be reckoned among the most fugitive, *e.g.* the eosines, which are metahydroxy compounds. The alizarines, orthohydroxy compounds, yield the fastest of all lakes.

The lake-forming bodies for the orthohydroxy compounds are the oxides of aluminium, chromium, and iron, which can play the part also of weak acids under certain circumstances. The lakes produced from alizarine by aluminium alone are by no means so brilliant as when calcium salts also enter into the lake-forming reactions. The exact nature of the lake formation with these dyes cannot be definitely stated, but it is to be inferred that the calcium and aluminium combine, with the aid of the oleic acid
which must be present to yield satisfactory results, yielding finally a calcium aluminium salt of the hydroxy colouring-matter. Aluminium lakes are those usually met with, but the corresponding lakes of both iron and chromium are of great permanency and value. The colouring-matters containing the carboxyl group, which may be regarded as an allied hydroxy group, yield but few colours which are used in the production of lakes. When present in the molecule with other hydroxy groups, and if these be in the ortho-position either in respect to themselves or the carboxyl group, these allied hydroxy groups possess the same properties as regards lake-formation as the diorthohydroxy dyestuffs.

When combined with several amido groups, the carboxyl group can generally be disregarded, and the colour treated as an ordinary basic colour. If both amido and hydroxy groups, as well as the carboxyl groups, or if the hydroxy groups, or a hydroxy and a carboxyl group, be in the ortho-position, the colour will be found to possess properties similar to those of the alizarines.

The sulpho group, which, like the carboxyl group, possesses no chromogenic powers, is found in the dye-stuffs together with hydroxy, carboxyl, and amido groups, both singly and in mixtures.

The sulphonic-acid group confers powerful acid properties on the colouring-matters, quite overpowering the basic properties of amido groups when they occur in the molecule, and greatly increasing the acid properties of other acid groups with which it may occur.

The increase in the number of sulphonic-acid groups in the molecule of a colour does not increase its lake-forming power, but the position of the sulphonic acid in the colour molecule has a very considerable influence on the lake-
forming capacity. Similar compounds prepared on the same lines, but with the sulphonic acid group in different positions, show marked differences in their behaviour with lake-forming bodies; and it must be concluded that the reason why many colouring-matters which apparently should yield lakes easily by combining the sulphonic-acid group with barium oxide, do not yield satisfactory results in practice, is because the intramolecular relationship is of such a character as to interfere with satisfactory lake formation. What these various relations are has not been studied, so that the constitution of the sulphonated dyestuffs used in lake-making should be carefully examined, and their behaviour with precipitating agents, and their reactions with acids and alkalies, both before and after lake formation has taken place, accurately noted.

The typical lake-forming body for the sulphonic-acid groups is barium oxide. Many of the oxides of other metals often precipitate more completely the colouring-matter, but the lakes lack both the brilliancy and permanency of the barium lakes.

The Hydroxy-sulphonic Acids.—The introduction of the sulphonic-acid group into a compound containing hydroxy groups. If these groups be not in the ortho-position in respect to each other, the weak lake-forming power of the hydroxy groups can be entirely overlooked, and lake formation takes place only in the sulphonic-acid groups. If, however, they be in the ortho-position, as in alizarine S, alizarine sulphonic acid, it will be found that, unless the hydroxy groups are combined as well as the sulphonic acid, the lakes produced are fugitive and lack the full development of the chromatic power of the colouring-matter. Since aluminium and allied oxides and hydrates are the lake-forming bodies for these groups, the aluminium barium
lake must be prepared, and the combination of one instead of both the lake-forming groups of the colouring-matter effected, otherwise the result is generally useless for pigmentary processes.

Although lake formation in dyes other than those in which the hydroxy groups are in the ortho-position may be, as a rule, disregarded, it is to be remarked that when the barium lake is formed in the presence of aluminium hydrate the resultant pigment is brighter and more permanent.

The introduction of the sulphonic-acid group into a basic dyestuff converts it into an acid dye, but it cannot be assumed that the lake-forming properties of the amido group are destroyed, for it will be found that the stronger the basic properties of the sulphonated base, the more difficult will it be to produce simple barium lakes from it. This difficulty is not solely dependent on the basic properties of the sulphonated colour base, but is often influenced by the molecular arrangement of the various groups.

It will be found that after the formation of the barium lake the basicity of the colour base again comes to the fore, and, unless this is also satisfied, the pigment produced will be found wanting in purity of tone and colour; in these cases, the only satisfactory lake-forming material to use is tannic acid, which develops the full beauty of the shade.

Though these dyes may be acid colours for the purpose of dyeing, when they are converted into the barium lake, which may be partially or wholly soluble, they must then be regarded as purely basic colours, and treated accordingly.

Basicity due to the presence of an amido group in a
sulphonic acid colour, of which the colour base possesses but very weak basic properties, as in the case of the hydroxy-sulphonic acids, in which the hydroxy groups have little or no lake-forming properties, often in these cases also loses its lake-forming power, and can then be disregarded: but in all cases where it, i.e., the basic lake-forming power, evinces itself, it must, if the best results be desired, be combined as well as the sulphonic-acid groups.

When hydroxy as well as amido groups possessing lake-forming properties are present in a colour molecule, it is often difficult to produce satisfactory lakes from such colours by means of tannic acid and barium chloride, because the hydroxy group, being uncombined, often renders the barium tannin lake soluble, and hence useless as a pigment; and unless the hydroxy group is combined by the use of an oxide or hydrate, with which it is capable of entering into combination, unsatisfactory results are only to be looked for. The hydrates of barium and calcium are most useful for this purpose.

Where a carboxyl group occurs together with both hydroxy and amido groups in a sulphonated colouring-matter, and the hydroxy and carboxyl groups are in the ortho-position, it will usually be found that the lake-forming property of the basic group will have disappeared: therefore, after the formation of the barium lake, the dye-stuff may be regarded as an ortho-hydroxy-carboxyl compound, and the compound lake must be produced by the means already discussed for such compounds.

The Azo Pigment Colours.—These, of themselves, cannot really be classed as lake colours; they are definite compounds formed by combining an amido compound with some suitable phenol by azotizing. They are very highly coloured bodies, of great staining power, and, like Prussian
blue, capable of being let down very considerably to form useful pigments. In some cases they can be used as pigments without any dilution. Many of these come into the market as the mono-sulphonic acids in combination with sodium, which the lake-maker simply substitutes by barium, calcium, zinc, or lead, according to the particular shade he requires.
CHAPTER VIII.

RED LAKES.

The various red shades of lake pigments derived from artificial colours vary from very yellow shades of scarlet to deep maroon. The colours from which they are formed belong to both the acid and basic dyes. The basic dyes belong principally to—

I. The triphenyl-methane colours, of which Magenta and Rhodamine are typical examples.

II. The azines, which are represented by the various brands of the Safranines.

The chief groups to which the acid colours belong are—

I. The azo colours, such as Scarlet 3R, Ponceau GL, Fast Red O.

II. The triphenyl-methane colours; for example, Eosine Phloxin.

III. The oxyketone colours, to which the Alizarine colours belong.

The most important of the red basic colours is magenta which is used not only alone to form lakes of a magenta-red shade, but with acid scarlets and reds to produce various shades of red. It is not of much use in modifying the shade of violet lakes, since its own pronounced shade interferes with the shade of the mixed colour lake, giving to it a harsh, unpleasing tone. The same fault also prevents it being used to shade eosine lakes, for which purpose the rhodamines, or rose Bengale, is to be preferred.
The brightest and most pleasing magenta lakes are those produced by combining the colour with arsenious or resinic acid. The tannic acid lake alone is not of any real value, being as fugitive as the arsenious acid lake, besides being very much duller. The tartar emetic and tannic acid lake is much more permanent, but not so bright as the arsenious acid lake, and though it is little in demand, on account of its inferior brilliancy, it has considerable use as a shading matter in producing the best qualities of maroon lakes. There is little to choose between the various brands of good magentas put into the market by the various firms; but it is advantageous to select a good crystallized variety and use it, and it alone, in all cases where a magenta is required. The rubin small crystals of the Berlin Company is about as good a one as there is in the market, though it is quite equalled by the production of other makers.

The rhodamines, of various brands, such as Rhodamine B, G, S, 6G, 12G, yield from bluish-red lakes to reddish-pink. When prepared alone, without admixture with other colours, it is by far the best plan to make the tartar emetic and tannic acid lakes, for lakes produced from any of these colours are extremely fugitive, and if the colour is wanted to stand the action of light at all, the tannic acid and tartar emetic precipitation is the only one which can be recommended. These lakes when prepared for calico printing should be made at the boil, and, after washing free from various salts, should be treated with a hot solution of 0.5 per cent. olive-oil soap at 80° C. The colours do not bleed, but the pigment then gives better results when printed. The best base to use is a fine quality of blanc-fixe.

The extra brand of the colour should always be used
when obtainable; though it is much dearer, it is more economical in the long run.

These colours, \textit{i.e.}, the rhodamines, are largely used for tainting violets; they are then precipitated with phosphoric acid or its salts. They are very powerful colours; a very small percentage, in the mixed colouring-matters, of a strong colour like Methyl-Violet B is sufficient to change the shade to a bright purple. It will be found that many of the red shades of violet are reddened merely by the addition of magenta. In lakes this does not give such pleasing shades as are given by the rhodamines, and it is advisable to use a pure methyl violet as the principal colour and to tone it with rhodamines. These colours are more expensive than the magentas, but, especially for surface paper-work, the shades given are much more attractive.

The rhodamines combine very readily with eosine, and when mixed with the eosine before precipitating with lead acetate, they blue the shade of the cheaper and yellower eosines, giving shades corresponding to those of a higher halogen, and, therefore, more expensive brand. In this conjunction the eosine and the rhodamine must be dissolved separately, and the rhodamine solution should be very dilute, otherwise there is risk of the two colours combining together in small specks, often so minute as not to be visible until the pigment is in use, as a very diluted tint, when the whole of the surface is covered with minute streaks.

The basic red colouring-matters of the azine group are represented by the various brands of safranine, which give a magenta-like lake, but one of a much faster and redder tone.

The only lakes of the safranines which are at all to be
recommended are those prepared from tartar emetic and tannic acid. These are much brighter than the corresponding magenta compounds, and, for purposes where superior fastness is required, are to be recommended. These colours are also of great value in making maroon lakes, since they do not give colours which blacken so readily when heated at 100° C. as those produced by magenta, more especially so when the basic colour is fixed, and not merely carried down by the acid colour.

For the safranines, as well as for all other tannic acid and tartar emetic lakes, the most suitable base is blanc-fixe. The safranines have also a considerable use, when precipitated as the resinate of aluminium, zinc, and lead, in stencilling inks and tin printing, since the shades are fairly fast to light and very bright. Also they lend themselves very readily to this form of precipitation. Recently they have been replaced by Ciba Red, which, though somewhat duller, is very much faster to light.

Coming to the azo group, it has been thought advisable to deal with the insoluble azo colours known as the pigment colours, such as Helio Fast Red RL, Pigment Red R, and the simpler sulphonic acids of similar compounds, e.g., Lake Red P, Lithol Red G and R, in the chapter dealing with the production of insoluble azo colours in the form of pigments, since the preparation of these colouring-matters for the market is practically a branch of the industry by itself, and the methods applicable to the ordinary hydroxy-sulphonic acids of the azo group are not suitable to them.

The red colouring-matters of the azo group are very numerous, and the number at the disposal of the lake-maker often causes the use of a very large number of brands, with resulting hesitancy in selecting colours to be
used to obtain a lake of a given shade. But the choice of colours should be strictly limited in practice; it is far better to obtain a shade by the judicious blending of a few scarlets or reds, than to buy for each separate lake a separate colour from which to produce it. Almost all shades of red and maroon produced from this colour can be obtained from a range of four to eight shades, i.e., four cheap and four better shades for the various classes of work, and the shades required may be classified as follows:

I. A yellow shade of scarlet, e.g., Ponceau 4GBL.
II. A medium shade, e.g., Ponceau GL and Ponceau GR.
III. A blue shade, e.g., Scarlet 3R, Ponceau 4R.
IV. A deep blue shade, e.g., Fast Red O.

The colours mentioned are but examples of many that are equally good and of similar shades and properties. In selecting a series of azo colouring-matters, attention should be paid to the following points:

I. The brilliancy and permanency of the pigment produced.
II. The colouring power of the dyestuff.
III. The insolubility of the pigments made from them in water.
IV. The complete precipitation of the colouring-matter.

The scarlets produced by the British manufacturer are fully equal to those of the continental firms.

Plate V shows a series of fairly wide range of acid scarlet dyestuffs which produce good lakes, these lakes are the barium lake on the clay or blanc-fixe alumina base:
PLATE V

Manufacture of Lake Pigments  To face page 90
Turning to the consideration of the constitution of the colouring-matters, the hydroxy-sulphonic acids are to be recommended. The more complicated azo-diazo colours obtained from benzidine, including the class of direct dyeing cotton colours, yield very good lakes; but, all things considered, the lake produced from the hydroxy-sulphonic acid colours are to be preferred, for, not only are they more permanent to light, but they are much more easily converted into pigments, and are as a rule much cheaper.

When using hydroxy-sulphonic acid colours, the best base is one containing aluminium hydrate, since the shades produced are much clearer and brighter when this body is present. If it does not enter into combination with the colour, it renders it much brighter and more stable. To give greater body, almost any inert material used as a base for lakes may be used, barytes, blanc-fixe, clay, etc.; but it is advisable to produce the aluminium hydrate in presence of the other members of the base, since it is then thoroughly incorporated with them, and a homogeneous base is the result.

The precipitating agent to be used for the majority of the azo-sulphonic acids is barium chloride. Soluble salts of lead very often give more complete precipitation, but the shades are much duller; the lead salts are much dearer than those of barium, besides being more readily changed by the action of air and light.

The best method of producing pigments from this class of red dyestuffs is by simultaneous precipitation with
barium sulphate or blanc-fixe, on a freshly prepared aluminium base, by means of barium chloride.

Lake pigments produced from a single colour will usually be found to have a bluish cast and lack brilliancy. This is best remedied by taking a colour which yields a lake of a much bluer shade than the shade required, and mixing it with a little orange dyestuff of a similar chemical nature, and precipitating in the usual way. It is desirable in this case, if the most fiery effects be required, to dissolve the colours together, for if they are dissolved separately, and then added to the tank, a slightly duller shade is the result. This also holds good as regards all the mixtures of these colours, whether they be reds or oranges. In the production of compound shades such as maroon, where basic colours are used, it is usual where the basic colour is not converted into a lake, but is merely carried down by the pigment formed from the acid-azo colour, to add the solution of the basic colour immediately after the addition of the colour to the base and before precipitation. On no account should basic colours and acid colours be dissolved together, for the result is usually disastrous, owing to the formation of a black or deeply coloured tarry precipitate.

In the production of the better sort of maroon and similar lakes, the magenta is introduced as a pigment. This is done by adding it to the base, and precipitating the red colouring-matter in the usual way.

For the production of maroon shades, basic brown (usually Bismarck Brown), magenta, and safranine are used to give the barium lake of the azo-scarlet the desired shade. The deeper the shade of maroon required, the deeper the shade the azo-red should be; but if such a colour as Fast Red O (M. L. & B.) be used alone, the shade
lacks brilliancy. It is therefore advisable always to use a proportion of bright scarlets in the mixture used for the production of maroons.

Maroon shades, made by utilizing the property possessed by acid colours of combining with basic colours, are much more fugitive than those in which the basic colour is introduced in the form of a pigment, and, as mentioned before, they have a tendency when dried at 100° C. to turn much deeper and blacker, losing all the bloom which such colours usually possess.

The acid red colouring-matters of the triphenyl-methane colours comprise mainly the eosines and allied colours. They are hydroxy colours. The hydroxy groups are not in the ortho-position in respect to each other, being usually in the different phenyl rings. They readily combine with the oxides of lead, zinc, aluminium, tin, etc., producing fugitive lakes of great brilliancy and staining power. The shade of the pigment produced is dependent on the metallic salt used in their production, lead salts giving the bluest, tin and aluminium much yellower shades. Barium salts do not react with those colours in a satisfactory manner, and the barium lakes are never prepared. The eosines, etc., all contain a large number of halogen atoms in their constitution, which probably influences to a great extent their attraction for the various metallic oxides, though the halogens themselves take no part in the formation of the lake pigments.

Of the eosines there are several brands—nearly every maker having a different name for the same compound, which, however, differ a little in the shade produced when made into lakes. For instance, a 5 per cent. lake on blanc-fixe made from Eosine A (of B.A.S.F.) differs somewhat from a 5 per cent. lake made from Eosine Yellowish (Ber.), yet both are salts of tetrabrom-fluoresceine.
Rose Bengal and the Phloxines are mixed halogen derivatives of Fluoresceine, which are rather expensive, but yield very bright and pleasing shades, of a much bluer cast than the Eosines proper. The introduction of iodine into the molecule tends to blue the shade of an Eosine, and many firms style the bluer shades of the fluoresceine colours Erythrosines. As a rule, these bluer shades are much more expensive than the yellower shades, which contain bromine or chlorine, and their price prevents the lake-maker using them. The method which is generally adopted to raise the shade of an Eosine is to add a little Rhodamine to the mixture of Eosine and base before precipitation; the Eosine combines with the basic Rhodamine, and the two colours are carried down together. In this case there is no advantage to be gained by using a pigment of Rhodamine, since the Eosine pigments themselves are so extremely fugitive.

The precipitation or production of eosine lake pigments is usually carried out either by lead, tin, zinc, or aluminium. They form the colouring-matter in vermillionettes and similar colours used largely for paint, and for this purpose are usually precipitated by lead acetate on barytes, lead sulphate, red lead, or mixtures of these bases. For paper-work and pulp colours, aluminium, tin, and zinc are used. Where an inert base is used, blanc-fixe is the only one really suitable; but mixed aluminium hydrate bases are largely used when aluminium and tin are used as precipitating agents.

Eosines, above all colours, are readily affected by the precipitating agent, and show very marked differences in appearance on the various substrata on which they may be thrown down.

Basic lead acetate gives the most perfect precipitation.
Normal lead acetate is almost as good, but gives a yellow shade, as might be expected; zinc salts give a light dullish blue tone, and the aluminium precipitation is the yellowest of all. The whole of these dyestuffs are very sensitive to acids, turning yellow at once with free mineral acids, and developing much bluer tones in the presence of alkalies.

The coarser the base the deeper and richer the pigment appears to be. On barytes and orange lead a very small percentage of colour gives a very full shade, whereas double the amount on precipitated lead sulphate or blanc-fixe is pale dull and chalky in appearance.

The selection of the brand of eosine to be used is a matter of some difficulty, since their prices vary from about three shillings a pound to over ten shillings; but it will be found that, by tinting the shade with basic colours of a yellower or bluer shade, any given shade can usually be obtained from any one eosine, whether it be a cheap or an expensive brand. Of the cheaper brands, Eosine A (B.A.S.F.) and Eosine GBF of Cassella are about the most satisfactory and reliable.

From the most easily manufactured and most fugitive lakes, it is now necessary to pass to the consideration of the most difficult lakes there are to manufacture, and the most permanent when properly made of all lake pigments, namely, the oxyketone colours, i.e., the alizarines, and allied ortho-dihydroxy colours, whether they contain other lake-forming groups or not. The remarks concerning these colours apply also to such colours as Gallein, Coerulein, etc., which, however, produce violet and green lakes.

Many and various recipes for the manufacture of these lakes are given, some of which yield lakes suitable for one purpose and unsuitable for another. It is not intended to go into the details of these methods, but to give an outline
of the most essential points to be observed in manufacture, which are applicable to the production of lakes from these colours by nearly all the methods.

The lake-forming bodies for these colouring-matters are the oxides of aluminium, iron, and chromium. These bodies alone do not yield lakes of great fastness or brilliancy, unless they are combined with calcium oxide, forming a double aluminium, iron, or chromium, and calcium salt. To obtain the brightest and most permanent aluminium lake, oleic acid or a similar body must be present. The exact composition of the lake cannot be accurately stated. The reds derived from the alizarine colours are among the most important of all lake colours and the most difficult to manufacture; as in dyeing, the brightest reds from these dyestuffs are those in the aluminium mordant, the brightest lakes are those in the aluminium base.

A study of the careful way in which cotton is mordanted for alizarine reds is of help in attacking this problem. It is one in which there is no royal road to success, for there is not the slightest doubt about the fact that what works well in the hands of one manufacturer is of no use in the hands of another, some slight unnoticed deviation causing the resulting product to be inferior to the exact article required, and it is only by careful study in the colour laboratory and then by careful attention to details in the colour-house that a constant and reliable product can be obtained.

In the first place the presence of even minute traces of iron in any one of the chemicals or materials used is quite sufficient to destroy the brightness and brilliancy of the lake, turning it dull and causing it to reduce to a dirty pink instead of almost as bright a reduction as that given by eosine. The presence of undeveloped dyestuff is also a great
bugbear. To avoid this there is only one safeguard, that is, to proceed very slowly in all stages of the manufacture.

The problem the lake manufacturer is set is not only to obtain a given shade or a given strength, but also to obtain a lake having the same physical characteristics as the sample, such as opacity, hardness, or softness, and similar working properties in oil and ink. With such a complex base as that of the alizarine lakes it is very easy to make a slight mistake, spoiling the whole of the resultant lake.

Where possible, until the lake is fully formed, it is advisable to use distilled water for all solutions. The aluminium sulphate should be very carefully tested for iron, and, if it cannot be obtained sufficiently pure for the purpose, potash alum should be used. There is considerable difference in the lake produced from potash alum and aluminium sulphate. It has been found impossible by the author to match an alizarine produced by potash alum by one produced by aluminium sulphate. Very close approximations were obtained, but they were much harder and more granular.

To eliminate the introduction of chlorides or acetates it has been found advantageous to precipitate the amount of calcium salt needed as phosphate, washing well and then taking same up in the solution of aluminium salt to be used to produce the lake with the addition, if necessary, of a little phosphoric acid.

Nearly every maker of alizarines gives one or more methods for making these lakes, all more or less useful. Each and all have to be modified and adapted to the particular lake the manufacturer has in view.

The most satisfactory lakes are made on the following basis: The alizarine is dissolved in a dilute solution of
sodium carbonate and sodium phosphate, the solutions being kept very dilute; alizarine oil, *i.e.*, sulphated olive oil, is then added, and the mixture agitated for several hours, during which a dilute solution of aluminium sulphate or alum is run in very slowly, the evolution of carbon dioxide never being allowed to become vigorous. After the addition of the whole of the aluminium sulphate, calcium acetate is added, also in very dilute solution; the mixture is left for a couple of days, being, however, occasionally stirred; heat is then applied and the whole mixture raised to the boil very slowly in about four hours, and boiled for about an hour and a half.

The formation of the aluminium alizarate may be assumed to take place at once; but the precipitation of the lake does not take place until heat is applied; and the decomposition of basic aluminium sulphate, formed on addition of dilute aluminium sulphate to the dilute alkaline solution, permits, during the time allowed, the formation of the complex calcium and aluminium base, with which alizarine yields its brightest shades.

Another method which is fairly satisfactory is to precipitate the aluminium hydrate first by means of sodium carbonate; wash quite free from all salts, then add the lime, phosphate, and turkey-red oil, and finally the alizarine in a thin cream, and boil for several hours. This method avoids the great frothing which always occurs with the first method and permits of smaller vessels being used.

Heating the lake in an autoclave instead of boiling is recommended. Better results, however, are obtained if the batch be first boiled, allowed to settle, the supernatant liquid decanted off, and the precipitate finished in an autoclave at about 60 lb. pressure for an hour, then thoroughly washed before drying.
The presence of compounds of phosphoric acid plays a very important part, for not only does it prevent the horny hardness of dry aluminium hydrate giving undesirable properties to the finished product, but, as we have seen in dealing with basic colours of the amido class, phosphoric acid compounds possess lake-forming properties when combined with aluminium. Alizarines being basic colouring-matters of the hydroxy class act also as one of the lake-forming constituents of the pigment.

When iron or chromium is used, the same method should be adopted, using a salt of the metal of which the lake is required, instead of a salt of aluminium.

These lakes for paper-work rather lack body, but are used for tinting purposes, yielding, when reduced, shades very similar to those produced by eosine, not quite so bright, but infinitely faster. When badly made, they are very much duller, and this has caused many stainers to look with suspicion on alizarine lakes.
CHAPTER IX.

ORANGE, YELLOW, GREEN, BLUE, VIOLET, AND BLACK LAKES.

The methods adopted to produce lakes of other colours than red are substantially the same as those described in the preceding chapter, attention being paid to the constitution of the colour, whether it be acid or basic, and the process for converting it into a lake pigment devised accordingly.

Orange lakes are principally manufactured from azo-sulphonic acids, since these yield much fuller and brighter colours than the basic oranges, such as the Phosphines. In conjunction with orange lakes, it is as well to note here that there are several of the azo-pigment colours giving various shades of orange, e.g., Fast Orange Paste of By, which merit consideration, but they are dealt with in the discussion of the other colouring-matters of that class.

Nitro-alizarine, or Alizarine Orange, is not used in the production of lake pigments, since the presence of the nitro group interferes with the ordinary methods used in the production of alizarine lakes.

There are a large number of orange dyestuffs in the market belonging to the azo group; they are mostly hydroxy-sulphonic acids, and, in the selection of orange dyestuffs, the same rules should be followed as those mentioned in the case of azo-scarlets.

The precipitating or lake-forming agent is therefore (100)
barium chloride, and the base aluminium hydrate, or a mixture containing a fairly large proportion of that body.

Of the various orange dyestuffs in the market, for cheap colours the Mandarins R and G (Ber.) give very satisfactory results; for an intermediate quality, Orange II (Basle) yields clear bright lakes. The extra qualities of the Brilliant Oranges O and R (M. L. & B.) yield about the most satisfactory results of any of the numerous orange dyestuffs.

In the production of cheap orange lakes, it is permissible to use a much higher percentage of clay in the base than with most colours. Orange lakes are largely made by precipitating a cheap orange on barytes, to produce imitation red lead; the orange lakes so made, however, are not very fast, and soon fade.

Brown lakes of various shades are principally derived from Bismarck brown by the formation of the tartar emetic and tannic acid lake in the same manner as similar lakes are prepared from basic red colouring-matters, the shade being modified by the addition of a red or blue basic colouring-matter as occasion demands.

There are a number of acid browns in the market which find considerable use in the manufacture of peculiar shades of brown which cannot readily be obtained from Bismarck brown and its congeners. They are mostly amido-sulphonic acids, and cannot be readily formed into good lakes by barium chloride, but must be also combined with tannic acid to produce the best result. In some cases this is not done, but a small quantity of a solution of albumin is run into the cold preparation and the temperature gradually raised to the boil.

The chromates of lead and zinc have for a long time made the production of yellow lakes, save for special purposes, of little or no interest. But, as in the case of the
pigment oranges and scarlets, the pigment yellows of equal
fastness and strength to the purely chemical colours above
mentioned have been introduced. They are of the usual
azo-pigment type and are discussed under that heading.

The yellow dyestuffs are principally used to modify
the shade of green lakes. The two principal basic yellow
colours are Auramine, a diphenyl-methane colour, and
Thioflavine T, a thiophenyl colour. There are numerous
acid yellows, of which Naphthol Yellow S, Metanil Yellow,
Quinoline Yellow, and Tartrazine, a hydrazine xylene yellow
(of Sandoz) colour, are the most useful for lake production.
Naphthol Yellow S gives a lake very fast to light but
which is soluble in water to a considerable extent and
can readily be detected when present in a lake by the
solution it gives with hot water. Metanil Yellow has the
same fault but to a lesser degree. Tartrazine gives deeper
shades which, however, are fairly fast to light. Quinoline
Yellow and Xylene Yellow give good lakes of a very pure
tone, the Xylene Yellow producing if anything the better
pigment.

Auramine gives a very good lake on blanc-fixe, suitable
for use in surface paper-work in place of lemon chrome,
where it is essential that the colouring-matter used should
be lead-free. Care must be taken in manufacturing this
lake not to boil it, or the colour, at any part of the process,
or the shade will be much deteriorated.

The two basic yellows, Auramine and Thioflavine T, are
both used in the production of greens from purely basic
dyestuffs, the Auramine giving a myrtle shade, the Thio-
flavine T the purer shade, but the latter is much the
more expensive.

A common method for the production of cheap green
lakes is to add a basic green colour to an acid yellow and
precipitate the two with barium chloride. This method cannot be too strongly deprecated, since it yields only fugitive shades, which, on drying or standing in the pulp state, after washing, dissociate giving the lake a mottled yellow appearance.

Naphthol Green S gives pigments which, though dull, are of the fastest to light and exposure generally produced.

Where purely basic greens are used, or where the pigment is formed by methods used for the precipitation of basic colours only, the basic yellows, Auramine or Thioflavine T (C.), should be used. The shade of the yellow used influences the shade of green produced.

With acid colours, Naphthol Yellow S is largely used for the production of pure shades of green; but when the yellow predominates in light shades, Quinoline Yellow and Xylene Yellow are to be preferred, since these give more delicate tints. Metanil yellow works well with greens used to produce the double barium and tannic acid lakes, since it contains an amido group; it yields sage-green tones of a peculiar cast.

Green Lakes.—Green colouring-matters occur in the triphenyl-methane group for the most part, and are either purely basic colours or sulphonated amido colours, the acid properties of which overcome the strong basicity of the numerous amido groups, but from which lakes can only be formed when both the amido and the sulphonic-acid groups have entered into combination.

From purely basic colours, such as Ethyl Green, Diamond Green, etc., the arsenious acid precipitation method gives by far the most brilliant results, the tartar emetic and tannic-acid lakes on any base appearing dull and insipid beside them.

When acid green colouring-matters are used, it will
often be found that barium chloride will give a fairly satisfactory green lake, more especially when an acid yellow colouring-matter is used to tint the colour; but it should on no account be forgotten that to produce the fastest as well as the most brilliant lake the amido groups which all these acid greens contain should be also combined with tannic acid and tartar emetic.

There is very little to choose between the brands of the various purely basic greens in the market. Preference, if any, might be given to the Ethyl-green crystals (Ber.), the Brilliant Green of (C.), and the Diamond Greens of B.A.S.F. Of the acid greens, of the many that the author has examined, the Acid Green D (Conc.) of M. L. & B. gives the most satisfactory results as regards both fastness to light and brilliancy of shade.

Coeruleine gives extremely fast shades of green, which are not made much commercially, since the process that must be adopted is similar to that used in the production of lakes from alizarine and allied colours.

Great use is made of the fact that many of the basic greens, especially Malachite Greens, combine with green earth directly, giving very fast shades to light, alkalies, and bleeding, and as the preparation of the green earth is improving, so are the pigments derived from them in the properties mentioned. It must be remembered in the production of this class of pigment, that the quality and properties of the green earth are of as much if not more importance than the colour or colours used.

Blue lakes for certain shades are largely used, but since they are derived from basic or sulphonated basic colours, they are rather fugitive, and mineral pigments, such as the ultramarines and the ferrocyanide compounds of iron, are preferred to them.
The colours from which they are derived belong chiefly to the triphenyl-methane group, the Oxazines, Thiazines, and Azines, and the purely acid blues of the azo group derived from benzidine.

With the basic colours the most satisfactory lakes are produced by tannic acid and tartar emetic, which yield full deep blues of rather a reddish tone. The purely basic blues of the triphenyl-methane group can be typically represented by—

\[
\text{Nile Blue, } \text{C} - \text{C}_6\text{H}_4\text{N(C}_6\text{H}_5)_2
\]

\[
\text{and Victoria Blue, } \text{C} - \text{C}_6\text{H}_4\text{N(CH}_3)_2
\]

The oxazines and thiazines by—

\[
\text{Naphthalene-Blue R (By.), } \text{Cl(CH}_3)_2\text{NC}_6\text{H}_3\overset{\text{N}}{\text{O}}\overset{\text{C}_10\text{H}_6}{\text{C}_10\text{H}_6}
\]

\[
\text{Nile Blue A (By.), } \text{Cl(CH}_3)_2\text{NC}_6\text{H}_3\overset{\text{N}}{\text{O}}\overset{\text{C}_{10}\text{H}_5\text{NH}_2}{\text{C}_{10}\text{H}_5\text{NH}_2}
\]

\[
\text{Methylene-Blue B (B.A.S.F.), } \text{Cl(CH}_3)_2\text{NC}_6\text{H}_3\overset{\text{N}}{\text{S}}\overset{\text{C}_6\text{H}_3\text{N(CH}_3)_2}{\text{C}_6\text{H}_3\text{N(CH}_3)_2}
\]

The Indulines by—

\[
\text{Neutral Blue (C.), } (\text{CH}_3)_2\text{NC}_6\text{H}_3\overset{\text{N}}{\text{N}}\overset{\text{C}_{10}\text{H}_6}{\text{C}_{10}\text{H}_6}
\]

\[
\text{Cl}\overset{\text{C}_6\text{H}_5}{\text{C}_6\text{H}_5}
\]

With tartar emetic and tannic acid on clay or blanc-fixe, these colours yield full deep fine shades of blue of a pleasing tone, but they all more or less tend to the red
side. To obtain pure blue shades, it is necessary to use the acid blues, i.e., the sulphonated basic blues, which belong mainly to the triphenyl-methane colours, and are well represented by—

Diphenylamine Blue, \( \text{C}_6\text{H}_4\text{NH} \cdot \text{C}_6\text{H}_4\text{SO}_3\text{Na} \)

Alkali Blue D (Ber.), \( \text{C}_6\text{H}_4\text{NH} \cdot \text{C}_6\text{H}_5 \)

Patent Blue BN (C.), \( \text{H}_2\text{O} \cdot \text{C}_6\text{H}_2\text{OH} \cdot \text{SO}_3\text{Na} \)

The Erioglaucine Blues of Geigy, derivatives of—

\[ \text{H}_5\text{C}_2 \]

\[ \text{H}_2\text{C} \]

\[ \text{H}_4\text{C}_6 \]

\[ \text{NH}_4\text{O}_3\text{S} \]

\[ \text{SO}_2 \]

\[ \text{SO}_3\text{NH}_4 \]

and Xylene Blue of Sandoz.

The first two are rather difficult to precipitate. In the case of Patent Blue BN a satisfactory precipitate is not obtained unless, as well as tartar emetic and tannic acid, barium hydrate is used to combine with the hydroxy group. In the case of Erioglaucines a little hydrate of zinc must be present in the base as well as aluminium hydrate, otherwise complete precipitation is not attained. The shade produced
from Erioglaucine A is a very pure azure blue, as also is the shade produced by Xylene Blue of the Sandoz Co., Basle, which has also the further advantage of being much more easily precipitated.

The production of a blue lake with a very high bronze and high staining power for lithographic work is made by combining together two such colours as Alkali Blue and Victoria Blue, and forming the lead salts of the sulphonic acids present by precipitating the combined colours with lead acetate.

The process is carried out in the following manner: 10 lb. of alkali blue are dissolved in about 200 galls. of water at the boil, 1½ lb. of 168° T. sulphuric acid added, then 5 lb. of Victoria Blue separately dissolved in 150 galls. of water run in, and finally 3 lb. of acetate of lead added in about 10 galls. of water; the mixture allowed to stand for thirty-six hours to cool and settle, the supernatant liquid run off, and the lake filtered off and dried at about 60° C. The essential point to be remembered is that the solutions, in all cases, must be very dilute. Washing is not necessary because of the small amount of materials used and the dilute nature of the solutions.

There is very little to choose between the brands of blue or the groups in which they occur. The acid blues of the azo group are not much used in the production of lakes, since equally fast and more brilliant blues can be produced from the basic blues and acid blues of the other groups, at a much less cost.

The deep blues that might be obtained from the alizarine blues have, in the form of lakes, little or no market, and are therefore not manufactured.

Violet lakes are produced mainly from basic violet colours which belong to the same groups of colours as the
blues just described. Where acid violets are used, the amidio groups must be combined with tartar emetic and tannic acid, and the sulphonic acid converted into the barium salt, if the full beauty of the colour is to be developed.

Purely basic violets give the brightest results when precipitated with phosphoric acid. The tartar emetic and tannic acid lakes are usually bluer in tone, but duller. They are, however, slightly faster than the lakes obtained by the phosphoric acid precipitation. The violets are often tinted with redder basic colours to obtain the desired shade. In all cases where softness of tone is desired, Rhodamine should be used, since Magenta or Safranine gives rather harsh shades.

The fastest violet lakes are produced from gallein in the same manner as the alizarine lakes. The shade is much duller than the violets produced from the basic and acid violets, but much faster.

Black lakes are mainly produced from the azo-acid colours. They are treated in the same manner as the azo-scarlets; since the shade they give in lakes is rarely ever a full deep black, but is of a bluish cast, they are often thrown down on a base containing a carbon black in the form of lamp, vegetable, or ivory black, the shade of which they modify. The pure lakes, however, are largely used for tinting purposes; but the lakes produced from logwood are much cheaper than those from the artificial colours, which consequently are not in much demand. The di-amino blacks, the black F.H.A. of Basle, and others give shades of black ranging from a bluish to a reddish shade. The indulines are largely used in the production of inks and stencil black, but very rarely as lakes—usually as the spirit soluble varieties.
Plate VI. shows some shades produced by both basic and acid dyestuffs ranging from reddish-yellow to black.

No. 1 shows Afghan Yellow R (Brit. Dyes).
No. 2 " Bismarck Brown Tannin Lake " "
No. 3 " Alkali Blue 2B " "
No. 4 " Soluble Blue 3M " "
No. 5 " Fast Acid Black H " "
No. 6 " Naphthalene Black B " "
CHAPTER X.

THE PRODUCTION OF INSOLUBLE AZO COLOURS IN THE FORM OF PIGMENTS.

The introduction of Primuline and of the method of dyeing ingrain colours by Green in 1887, by which the amido groups of the Primuline were diazotized after dyeing on the fibre and then combined with an amine or a phenol, led to the introduction of a large number of colours capable of being treated in this manner, together with the process of impregnating cotton with a solution of a phenol and producing an insoluble azo colour by passing it through a solution of a diazotized compound.

Of recent years, owing mainly to the general fastness of the colours so produced, this process has been applied to the production of pigments by the formation of insoluble azo colours on suitable media, more especially those of a red colour. These products cannot be regarded in any way, however, as lakes, but rather as strong pigments diluted in the process of formation by suitable substances, to make them of service as paints and colours for allied work.

Very few dyes are used for this purpose, for, apart from primuline, the colours produced from dyes are browns, blues, and blacks, which colours produced from coal-tar products are but little in demand; and the red shade produced from diazotized primuline and β-naphthol is very little superior to that produced more easily from an ordinary azo-sulphonic acid.

(110)
These pigments are therefore produced almost entirely by diazotizing an amine and then combining it with a phenol or amine in solution, in which is suspended the base or bases which it is desired to colour.

There are several methods in use, the principal being the simultaneous production of the azo colour and the resinate or phosphate of zinc or aluminium, by adding to mixed solutions of a phenol or amine and the sodium salts of either resinic or phosphoric acid, a diazo solution containing salts of either aluminium or zinc. Meister Lucius & Brunning strongly recommend the use of resinate of soda; but pigments containing resinates do not work at all well in oil, and, for pulp colours, though very bright, they are apt to work thin and transparent.

With the azophor reds of the above-mentioned firm, pigments of fair brilliancy and of soft easy-working texture have been obtained, by using sodium sulphate along with the solution of the naphthol, and barium chloride with the diazo solution.

Previous to the closing of the main continental source of the artificial colouring-matters, there was available a long range of shades, from a pale lemon of the Pigment Yellows to the almost crimson of Permanent Red 3B.

They were divisible into two classes, those which were a combination of amines and naphthols, and those which contained a sulphonic-acid group. The former were used simply as pigments of high staining power, and ground into the base either in the dry or in pulp, being afterwards dried and ground, or otherwise prepared for market. The sulphonic acids were for the most part very slightly soluble salts, and were sold usually as stiff pastes containing 20 per cent. of colouring-matter, but sometimes as the dry powder. The shade was developed and modified by
substituting the sodium in the sulphonate by barium, calcium, zinc, or lead, each of which modified the shade somewhat, giving it a bluer or a yellower cast as the case might be; barium and zinc gave the yellower tones, lead and calcium the bluer ones. In some of the deeper shades, manganese sulphate gives the best shades of all.

The fastness to light of these colouring-matters varies from poor in the case of Paranitraniline Red, to medium in the case of Lithol Reds and fairly good in that of Helio Fast Red RL. Some are more soluble in benzol than others. All those that are not salts of the sulphonic acids are soluble in hot benzol. The sulphonic acid salts are not soluble, and this gives a ready method of testing which class of these colours is being dealt with. They also vary in their solubility in various media, such as linseed oil, turpentine, white spirit, and alcohol, so that they are prone to bleed when light colours in these media are painted over them. In such cases it is advisable to paint them over with several different mixtures containing a white or very light pigment, before guaranteeing them fast to bleeding.

The manufacture of these colours is very simple, yet it should be carried out with care if the best results are to be obtained.

In grinding the colouring-matter into a dry base, such as barytes or blanc-fixe, it is better to incorporate thoroughly only a portion of the base with the whole of the colouring-matter, adding the remainder of the base little by little.

A little mineral oil is often used to bring up the colour. Above 2 per cent. of the total weight of the charge, this is not advisable. A much smaller quantity than this can be used if the oil be dissolved in a little benzol before use.
The latter is fairly volatile and volatilizes during the grinding, leaving the heavier oil very much more evenly distributed throughout the whole mass, and, since many of the azo colours, as has already been stated, are soluble in benzene, this reagent, by partial solution, helps to bring up the shade more rapidly. Great care must be exercised both in respect to the quantity used and the proximity of naked lights, since the vapour of benzene is highly inflammable.

Where pulp azo colouring-matters are used, it is advisable to incorporate thoroughly the pulp colouring-matter with the base, and afterwards to drive off the excess of water before grinding and finishing in the ordinary way.

With paste and dry colouring-matters of this class, which require the addition of barium or calcium salts to develop the shade, it is by far the best method to break down the required quantity of the pulp into a thin cream with water, sieve into a suitable tank or vat through a 20-mesh sieve, raise if necessary nearly to boiling, run in the base with more water through a sieve of similar mesh, stirring the whole time, and then to add the requisite quantity of the barium or other salt. If the shade requires boiling—necessary in some cases to produce an alteration or a further development—boil for the required time. Finally, fill up with cold water, allow to settle, and wash by decantation once or twice according to the amount of pigment present.

Adding the barium or other salt to a thick mixture in a pan mill, or working with too thick mixtures of the colouring-matter and base, may increase output and the speed with which the work can be done, but the product is much inferior in quality, and is nearly always but
partially developed, giving rise to faults and complaints as to the constancy of shade and the reliability of the pigment.

The combinations of the diazotized amines with the various phenols and amines, to produce these colouring-matters, are mostly patented. In the transient stage of the dye-making industry in this country it is to be recommended to the pigment manufacturers that they obtain a licence to use these methods, and prepare their own colouring-matters from the intermediate products. They will not be able, at first, to produce so fine a quality of material as the original makers, nor will their product be quite so constant owing to variations in the intermediate products, but the pigment manufacturers will be able to satisfy their own requirements, and to relieve the pressure on the British dyestuff manufacturing firms until these are in a position to cater for their requirements more cheaply than they can make the required substances themselves.

A careful study of the reactions and the chemical nature of the various phenols and amines used will show that, if the physical requirements of the production of these colouring-matters be carefully attended to, little difficulty will be experienced in manufacturing them.

Plate VII.—The behaviour of these colouring-matters is shown in Plate VII, which shows Lake Red P of British Dyes:—

I. On Barytes.
II. .. Blanc-Fixe.
III. ,, China Clay.
IV. ,, Barytes and Alumina.
V. ,, Blanc-Fixe and Alumina.
VI. ,, Clay and Alumina.
The reactions involved are well illustrated in the production of the best known of these colours, *viz.*, Paranitraniline Red, which is produced by combining diazotized paranitraniline with $\beta$-naphthol.

Paranitraniline $\text{C}_6\text{H}_4\left[\text{NO}_2\right]_\text{NH}_2$ is a bright yellow powder of a crystalline nature, which is very slightly soluble in water, but soluble in hydrochloric acid, producing the hydrochloride. This salt is fairly soluble in boiling water, but unless the solution be very dilute it is reprecipitated on cooling; 1 to 2 per cent. solutions only do not deposit on standing. The aqueous solution of the hydrochloride has a clear yellow colour, which turns slightly browner when the nitrite of soda is added, owing to the amido group being converted into the diazo group. Thus—

$$\text{C}_6\text{H}_4\left[\text{NO}_2\right]_\text{NH}_2\text{HCl} + \text{HNO}_2 = \text{C}_6\text{H}_4\text{N : N : Cl} + 2\text{H}_2\text{O}$$

The paranitro-azo chloride is very unstable, readily decomposing above 50° F. with the evolution of nitrogen, which together with the deepening of the colour indicates that for the purpose of pigment-making the preparation is wasted. A slight deposition of the hydrochloride in the original paranitraniline solution, before the addition of sodium nitrite, may be ignored; but, unless, before decomposition sets in, the insoluble matter has entirely disappeared, it is useless to proceed, since specks of yellow will pervade the resulting pigment, and the colour produced will be dull and unsatisfactory.

The diazotized base, when run into a phenol or an amine solution, readily combines with it, producing a stable coloured compound. Thus—

$$\text{C}_6\text{H}_4\text{NO}_2\text{N : Cl} + \text{C}_{10}\text{H}_2\text{ONa} = \text{C}_6\text{H}_4\text{N : NC}_{10}\text{H}_6\text{OH} + \text{NaCl}$$
Various makers of paranitraniline give recipes for the preparation of these pigments, nearly all of which produce excellent results if carefully carried out with pure chemicals; but, commercially, where the materials used at one works differ a little from those used at another, adaptation of details to existing conditions is essential. It is, therefore, of little value to give minute instructions for the production of these pigments, since considerable practice is necessary to obtain really good results. A good plan is to work out carefully, with pure chemicals, some recipe such as the following, and to apply to it those corrections rendered necessary by impurities in the ordinary supplies:

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthol mixture</td>
<td></td>
</tr>
<tr>
<td>224 parts blanc-fixe</td>
<td></td>
</tr>
<tr>
<td>2·5 βC₁₀H₁₂O₆H</td>
<td></td>
</tr>
<tr>
<td>0·7 NaHO</td>
<td></td>
</tr>
<tr>
<td>2·5 Na₂CO₃</td>
<td></td>
</tr>
<tr>
<td>1·0 oleine</td>
<td></td>
</tr>
<tr>
<td>Diazomixture</td>
<td></td>
</tr>
<tr>
<td>2·4 C₆H₄NO₂NH₂</td>
<td></td>
</tr>
<tr>
<td>6·0 HCl 1·2 sp. gr.</td>
<td></td>
</tr>
<tr>
<td>1·22 NaNO₂</td>
<td></td>
</tr>
<tr>
<td>250 water</td>
<td></td>
</tr>
</tbody>
</table>

On examination the reagents in this recipe will be seen to be in molecular proportions, and, unless the mixtures when added together give an almost neutral or preferably slightly acid mother liquor, the resultant pigment will be disappointing. In the presence of an excess of mineral acid, the colour, instead of being bright red, is brickish, and, with alkali, dull and dirty. The presence of a little acetate of soda in the naphthol mixture is advisable, since the presence of acetic acid has not, even in fairly large quantities, the deleterious action of free hydrochloric acid.

These colours are easily made when attention is carefully paid to detail, but the details cannot be given, since they differ under various conditions, and are only
to be learnt by careful experiment and close attention to the chemistry and behaviour of the materials used, and of the intermediate products formed in the course of the operation.

The following are some of the principal naphthols and amines used to combine with the various diazotized bases:—

- **β-naphthol.**
- **α-naphthol.**
- **Diphenylamine.**
- **Resorcinol.**
- **Phenol.**
- **β-naphthol disulphonic acid.**
- **m.-phenylene diamine.**
- **α-naphthol sulphonlic acid.**

They are often sold under the name of developers, and are then usually prepared for use by combination with sodium in the case of phenols, and with acids to form salts in that of the amines.

Among the chief bases that are diazotized are—

- **m. and p.-nitraniline.**
- **p.-phenilidine sulphate.**
- **o.-nitro-p.-phenilidine.**

The various azophor reds, etc.

**Plate VIII.—** The influence on the shade caused by the base, and the influence of the base on the reduction on these pigment colours is shown in Plate VIII which shows:—

I. Lake Red P on Barytes.
II. Lake Red P on Barytes reduced 1 : 20 with white.
III. Lake Red P on Blanc-Fixe.
IV. Lake Red P on Blanc-Fixe, but reduced 1 : 20 with white.
V. Lake Red P on Orange Lead.
Lake Red P on Orange Lead but reduced 1 : 20 with white.
CHAPTER XI.

THE GENERAL PROPERTIES OF LAKES PRODUCED FROM ARTIFICIAL COLOURS.

The physical properties of lake pigments depend on their two main constituents—the lake itself, and the base on which it is struck or with which it is combined.

The nature of the base, whether it be in a fine state of division or in coarse particles, e.g., blanc-fixe and barytes, alters very considerably the appearance of the lake. It may be taken, however, as an axiom, that the coarser the base the fuller and richer is the appearance of a lake struck on it; the finer the particles of the base are, the paler and duller will the product appear. This difference is the more noticeable in dry pigments and in those used as water colours. With pigments in oil, or in preparations containing oil, it is still very distinct but not quite so marked.

The covering power of a pigment is nearly always dependent on the base. In alizarine lakes, with arsenious and phosphoric acid compounds as bases, the pigments are nearly transparent in oil. Most of the pure lakes themselves possess little or no covering power, and very little opacity. The nature, however, of the precipitated lake exerts a marked influence on this property. Lakes that come down as flocculent precipitates usually have very little influence on the body of the pigment, those that come down as amorphous powders greatly increase it. Those
pigments in which the base is precipitated or partially precipitated with the lake usually possess greater covering power and opacity than those merely struck on an inert base.

It will be found, more particularly in the case of the azo sulphonie-acid colours, that the amount of lake cannot be increased with advantage beyond a certain percentage, because the lake when dry becomes so hard and horny that the full value of its colouring power cannot be made use of, and it will not work up as a paint or ink in oil or varnish. However, in the case of the simple azo pigment Helio Fast Red RL, the pure pigment itself is very readily worked up as a paint, and can therefore be used in all percentages in the production of pigments from various bases.

It cannot be assumed that the covering power, density, opacity, and staining power are dependent solely on the base, and almost every lake requires consideration and modification to produce the best and most economical pigment from it. It is only by repeated trials that the most suitable base and precipitating agents can be decided upon for any individual colour. A pigment well suited for linoleum work may be of no value for the preparation of lithographic ink. The nature of the precipitate when just struck, and when washed and ready for the filter-press, the rapidity or otherwise of its filtration, the nature of the cakes in the filter-press, whether they be homogeneous or hard on the cloth and soft in the middle, often give very good indications as to what the finished dry pigment will be, and the study of these details frequently enables an experienced hand to modify and adjust some little point, thereby correcting a fault which would impair the value of the pigment, before it is too late.

*Staining Power.*—The same percentage of a colour
struck on barytes and blanc-fixe, say 5 per cent. of an eosine precipitated with acetate of lead, will yield colours very different in appearance and shade, yet, on reduction in white, it will be found that the finer base gives the stronger staining lake. This can be accounted for as follows: The larger particles of the coarse base are more thickly coated with the lake since they expose a much less total surface to be covered than the same weight of the finer material: in the latter, the colouring-matter is spread over a greater surface giving a paler resultant, but one which, on account of its greater original extension, can impart a deeper tint when reduced.

In cases where the pure lake has a tendency to dry in hard horny masses, care should be taken that too great a percentage of the lake be not present in any pigment made from it, otherwise, after drying, the pigment will have much less staining power than one containing a smaller percentage of lake colour.

In the production of lake pigments for staining, the object of the maker is to produce, at the least cost, a product with the maximum staining power. This can only be done by careful selection of the base and the amount of colouring-matter to be used.

As a general rule, lakes that are to be used as self-colours in paint work are required full and bright of shade in oil. The question of their strength on reduction is not one of importance. It is wise in this case to use heavy and coarse substrata, but where staining power is a desideratum, the lighter and finer the base used the better.

It will be found that lakes made from the alizarine dyestuffs and the basic amido colours, such as Bismarck Brown and Malachite Green, possess the greatest staining power.
Pigments produced from artificial colouring-matters, with the exception of those obtained from alizarine and its allies, and from azo colours prepared by combining a diazotized amine with a naphthol or an amine, are not fast on exposure to light, air, and moisture. Their fastness varies, but the most fugitive are usually the most brilliant, and give the most pleasing shades; hence they are largely in demand. Among the best examples of the most fugitive lakes are those obtained from the Eosines, and the triphenyl methane basic colours, such as Ethyl and Methyl Green, Magenta, Nile Blue, etc., which six hours' exposure is sufficient to alter to a marked extent. The scarlets and greens obtained from the azo colours vary in fastness, but are relatively much faster than those previously mentioned. The faster colours are those which are double and triple lakes, and not merely precipitated colouring-matters. Safranines yield fairly fast tannic acid lakes, but they lack brilliancy, otherwise they would largely displace the arsenious lakes of Magenta, to the shade of which they approximate.

The media in which the lakes are used greatly affect their fastness to light, air, and moisture. When the colours are used with size, fading is the most rapid; in oil and lithographic ink the alteration is not so soon evident. A lake was made from Orange II, and three strips painted on a piece of glass—

1. the pulp in size,
2. the dried colour, in oil,
3. the dried colour in lithographic ink.

All were exposed to the action of light, air, and moisture. After three days

1. had faded to a dirty brown,
2. and (3) had lost but little brilliancy.
Ten days' exposure was necessary to render (2) and (3) of the same shade as (1) after three days' exposure, (3) taking slightly the longer time.

It will be found that a very short exposure to direct sunlight, say twelve hours, rapidly deteriorates the brilliancy of the colour, after which the shade changes with more or less rapidity; oranges and yellows become dirty and brownish; scarlets, crimsons, and cardinals darken and become much bluer; magentas, violets, and maroons blacken with an entire change in shade; greens become bluer, and bleach with great rapidity.

In testing the staining or colouring power of a dry lake, it is better to use a good linseed oil and white lead, but what holds good for a pulp colour will be found to hold good with the dry colour. It must be remembered that though a lake may be matched to work in size, it may not match when worked in other media. In a case where an imitation vermilion was required in a great hurry, the shade was matched to a nicety with an eosine and an orange, when both the sample and the match were tested by rubbing out on paper with a little size; but when they came to be tested one against the other in oil, the shade given by the eosine-orange match was much too deep and red, and the pigment had to be made with entirely different colours.

There can be no fixed percentage given for dry colour in pulp colours since the various classes of lakes vary greatly in pulp-forming properties. Care should be taken to ensure that, if a lake gives satisfaction, when containing a certain percentage of dry pigment, it is always maintained at that percentage, for, if it be sent out containing more than the usual percentage, it will not be usable, since it will not fall down and work easily in size, and, if
containing a greater proportion of water, it will work far too thin. A rough method of testing whether a pulp pigment be in proper condition is by stirring gently two ounces of it in a vessel with about an ounce of prepared size, by means of a stick or glass rod. If the lake has been properly made and is in proper condition, it will give, with very little agitation, a creamy homogeneous mixture with the size.

Many lakes are partially soluble in boiling water, a property of which advantage can be taken when the shade of a lake is a little too deep and it is desired to render it paler, an operation that cannot be satisfactorily carried out by increasing the amount of base present when once the lake has been made. Though boiling leads to a little loss, such loss is preferable to the risk of spoiling the whole product by additions which would demonstrate their presence in the finished pigment. The addition of soda, oil, or soap to increase the solubility of the lake cannot be too strongly condemned, since the beauty of the pigment is nearly always destroyed.

Some pigments being soluble to a slight extent in hot water, when struck at or near the boil a considerable amount of the lake is dissolved. It is advisable in such cases, before syphoning off the supernatant liquor, to allow the whole to become quite cold. With occasional stirring, practically all the lake is obtained in the pigment, and, in addition, a considerable increase in brightness of the finished product results.

The solubility of a lake in water has certain drawbacks, among which is the fact that such a colour cannot be completely precipitated. The necessary washing increases the loss, and, in use, the colour bleeds, rendering it unfit for use for many purposes.
Bleeding, however, can be caused otherwise than by the solubility of the lake; for, in a case that came under the author's notice, where a batch of colour had been made in a tank that was only fitted for making half the quantity, the wash waters came away quite clear, with the result that more washing than usual was given; but, when the colour came to be used in size for surface papers, it bled so frightfully that it was of no use, yet previous batches made in smaller quantities at a time, and deliveries since made correctly have not behaved in this manner.

For pulp colours a pigment should settle, after digestion with water for three hours at 50° C., leaving the water quite clear, or but very slightly tinged; dry pigments should also be similarly tested in alcohol, glycerine, and turpentine.

The action of heat in some cases causes the shade to alter materially. This is very noticeable in those maroons made by a combination of Magenta and some blue shade of scarlet, more especially where the Magenta has not been fixed otherwise than by its property of combining with the Acid Scarlet; in some Ponceaux, such as Ponceau 4 RB (Berlin), and in greens precipitated by arsenious acid with which great care has not been taken. As a rule, a good lake can be dried at 100° C. without undergoing any change, but, generally, lake pigments should be dried in a current of air at a temperature a little over 50° C. If they change in drying much below 100° C. the conclusions to be drawn are either that the colouring-matters have not been properly combined to form true pigments, that an inferior grade of dye-stuff is being used, that an irrational mixture of one or more incompatible colouring-matters has been used, that some error has crept
in during the striking, or that the colour has been improperly washed. The use of too concentrated solutions of the dyestuff is frequently the cause. Again, an insufficiency of the precipitating agent sometimes gives rise to this defect.
CHAPTER XII.

STRIKING, WASHING, FILTERING, AND FINISHING.

The correct dyestuff, base, and precipitant may be assembled, but unless the lake be struck properly the result will be unsatisfactory.

In making or repeating batches of the same lake pigment, it is very necessary, as far as possible, to strike them exactly in the same way and under the same physical conditions. The points which need most careful noting are:—

1. To have the solutions always of the same strength, and when, after solution, the material is diluted, to dilute always to the same extent.

2. The temperature at which the lake pigment is struck should be noted, and all subsequent batches struck at this temperature. The solutions or mixtures that are added should be at approximately the same temperature.

3. The order of addition of the various colouring-matters and chemicals should always be the same.

4. The time taken in making these additions, and the rate at which they are prepared, should not vary.

5. The stirring or agitation of the mixture while in process must be exactly the same in all cases.

Dyestuffs and colouring-matters from reliable firms can generally be taken as equal to standard, but, if possible, it is advisable to test them. All chemicals, such as aluminium sulphate, soda ash, barium chloride, barytes (126)
clay, acids, etc., should be invariably carefully tested to ascertain whether they are of the purity and strength required for the formula to which the lake is being made.

It is most unwise to vary any conditions after once they have been settled, if succeeding batches of pigment are to be identical, for, on the physical conditions under which the pigment is made, the physical properties of the product depend, and often the slightest deviation from these conditions results in variations from the standard, rendering the material quite unserviceable.

Doubling the quantities used when pressed for time and large quantities are required, is a foolish policy, for the whole conditions of the precipitation are thereby altered, and the product cannot be relied upon to be the same as one prepared under normal conditions.

Increasing the time allowed for washing, especially in the case of highly aluminous precipitates, is unwise, since occluded salts diffuse from aluminium hydrate only with difficulty.

It is not advisable to use too large tanks or vats; ascertain the maximum capacity of each striking vessel, and work always with that amount.

Mechanical stirring is to be preferred where heavy substrata are used, but, unless this is very easily controlled, in cases where there is much effervescence at any stage of the manufacture, hand stirring should be resorted to.

Tanks or vats having a capacity of about 1000 gallons are of convenient size for making 4 to 5 cwt. of dry lake on a blanc-fixe alumina base, or about \( \frac{1}{2} \) ton of pulp lake.

However pressing requirements may be, the lake manufacturer, having once ascertained by experiment the minimum time required and the maximum quantity of
lake he can make with the materials and plant at his disposal, is only seeking trouble if he varies from these in the slightest degree.

One of the most important operations in the manufacture of lakes is the washing, or the removal of those soluble by-products produced during the various operations. Unless these are entirely removed, it is useless to look for the fullest and brightest shades; and, further, owing to their action on the various media used in their application such by-products frequently render the pigments of little value. It will be found that, in at least 50 per cent. of the cases where complaint is made against a delivery of a pigment, the cause arises from defective washing.

The operation of "washing" may be carried out in two ways, either by the use of a filter-pump which filters and washes the colour simultaneously, or by decantation. The first method is the more rapid, and is extremely effective where the pigment is of an open and granular texture, e.g., such as imitation red lead, or vermilionettes; but, in colours of a more gelatinous nature, especially high-class lakes sold in the pulp form, it is a better plan to wash by decantation, since time is required to enable the impurities retained in particles of the lake to diffuse into the wash water. Experience has shown that, in some cases, where, owing to urgency, one part of a batch of colour has been washed in a filter-press, it has been rejected, while the other part washed by decantation has given every satisfaction. The purpose for which the pigment is required determines to a great extent the process of washing to be adopted. Colours for use in oil, i.e., pigments used by paint grinders, linoleum manufacturers, lithographers, etc., can be effectively washed by the filter-press; but with high-class lakes, more especially those used as pulp colours, and containing
a high proportion of hydrate of aluminium in the base, it is safer to wash by decantation.

Most colours settle completely in about eight to ten hours, but the speed of settling is entirely dependent on the nature and texture of the lake in hand, heavy base lakes settling in much less time than those containing a lighter base. It will also be found that many lakes settle rapidly and clearly with the first water, but much more slowly with each successive washing. This is not due to any action of the water on the lake itself, but to the fact that in the saline solution the pigments settle better, and, as the soluble matter is eliminated by each successive washing, the lake settles with less rapidity.

When washing by decantation, it has been found to be advantageous to arrange that the bulk of the settled precipitate is about 25 per cent. of the capacity of the tank or vessel in which the colour is made. Three times washing in such a case will be found quite sufficient; for, supposing the soluble impurities of a batch to be represented by 100, the first water taken off removes at least 75 per cent., leaving less than 25 per cent. in the tank with the lake, the second leaves less than 6.25 per cent., and the third less than 1.5625 per cent., fully two-thirds of which is subsequently removed by filtration and pressing.

In cases of urgency, it is advisable, when the salts, etc., in solution have no action on the pigment, to allow as long as possible for the first washing since this water contains the greater proportion of the impurities it is desired to remove; and it is better to take off one water after complete settlement than to remove two or three after partial settlement. As a general rule the first water should be removed as soon as the pigment has well settled, but, in cases where the precipitate being washed is of a gelatinous
nature, *i.e.*, those containing a high proportion of colouring-matter or aluminium hydrate, it is advisable to allow the second water to remain as long as possible, in order to allow the soluble matters entangled in the particles of the lake time to diffuse into the wash water.

When a lake "hangs," as it is termed, in the colour house, *i.e.*, does not settle completely with the last water, leaving a haze of more or less density, the practice of adding a little soda or alum to clear the liquid is to be deprecated, since, in nearly every case, this addition injures the pigment, and the loss caused by running off the haze together with the last water is usually very small. It is wiser to suffer this loss than to spoil the lake by tampering with it.

In cases where the lake refuses to settle with the first water, it will be found that there has been some error in the manufacture, and whether that error can be corrected depends on the nature of the lake and the extent and action of the mistake made.

The filtration of the pigment after washing is completed can be carried out in several ways. For dry colours, the filter-press is the best method to adopt, since it can be regulated to give the pressed and filtered pigment in such a state that it requires but little time to dry completely.

Vacuum filters can be very cheaply and easily fitted up in those cases where the outlay involved in putting down presses is objected to, the vacuum being produced by an ejector or the condensation of steam. The figures on next page will illustrate their general construction.

The method of using either of these forms can readily be grasped. The perforated plate C is carefully covered and packed, to avoid leakages, with a stout covering of calico. The matter to be filtered is poured on until the cylinder marked U or U' is about half filled. The taps
STRIKING, WASHING, FILTERING, AND FINISHING. 131

T' and T are closed. Where the ejector is used, high-pressure steam is admitted to it, when it withdraws the air from L', creating a vacuum into which the filtrate rapidly runs, a pressure of 15 in. being readily obtainable. The steam and valve VN are both shut off at the same time, the filter being left until the vacuum is nearly exhausted, and the process repeated until the filtering process is completed.

Figs. 1 and 2.—A and A', 1/2 in. iron. B and B', Flanges to support C and C'. C and C', 1/4 in. perforated iron plates. T and T', Taps to run off the filtrate. V V' V'', 1/4 in. valves. G and G', Vacuum gauges. L, Condensation chamber, 1/4 in. iron cylinder with steam inlet through V, outlet through B, and connected with A by means of iron pipe N, which can be opened or closed by valve V'. L', a steam ejector connected with boiler by pipe S, and the air by outlet H, and with A by the tube N'.

When the vacuum is produced by the condensation of steam, the cylinder E is shut off from the filter A, and the air driven out by live steam, through valve V. When nothing but steam issues from valve V', the steam is shut off at V'' and V closed simultaneously, allowing the cylinder to cool partially. The connection with A is made by U on valve V', which connects the lower portion of A with E. The condensation of the steam in E produces a partial vacuum, which often indicates as much as 20 in., and the filtration proceeds rapidly from U through C into L.

Both these filters work very rapidly, the only objection being that toward the end of the operation the lake
frequently stiffens too much at the bottom, giving pulp colours rather an uneven and lumpy look; but in the case of dry colours they work very well and economically. Neither filter-presses nor vacuum filters, unless the iron is well protected from the action of the lake, should be used for colours which act on metallic iron, e.g., tannic acid lakes, which are blackened and discoloured by such contact.

For pulp colours of a high class, it is perhaps better to proceed slowly by filtering in "open filters," i.e., calico spread on wooden frames. This operation requires from a couple of days to a week to complete, and, when complete, a slight finish is usually given in a hydraulic press. The method, though tedious for many lakes, gives a much more homogeneous paste which readily breaks down in size.

Lakes are sold both as pastes and dry. The percentage of moisture varies from 60 to 40 per cent. in pulp colours, and great care should be taken to send out any given pulp always with the same percentage of moisture. Most of these pastes are used with size, and, if the lake contain too much water, when it is used, it appears to lack body, and is transparent; if too dry, it thickens the size too much, rendering it unusable, since the addition of more size would alter the shade and appearance.

Dry colours are sold in lumps, "drops," and powder. When lumps are wanted, it is customary to break the dried lake roughly. "Drops" are made by forcing the pressed lake, after it has been mixed with a little gum, through machines devised for that purpose, the gum being added to bind the particles together, so that they will retain the form given them by the machine, when dried. Similar machines exist for producing lumps of a definite shape, in which case also a little gum is added before the product is sent to the machine. When a lake has to be powdered, it
is not advisable to press it too hard or to dry it too quickly, since such treatment diminishes the friability, and renders grinding more difficult.

Where large quantities of barytes have been used, the last portions removed from the striking tank frequently contain a much greater proportion of barytes than the bulk of the product. It is advisable to grind roughly the whole batch, distributing this portion throughout the whole grinding, before proceeding to grind for the finished article.

The use of a mineral or castor oil for improving the appearance of a ground colour is better avoided if possible, but, when appearance is a great consideration, it may be used, but not to the extent of more than 2 per cent. If added in some volatile solvent which volatilizes during grinding, the oil is better distributed, and much less oil gives the desired effect. More than 2 per cent. of oil has a tendency to cause the powdered pigment to cake, but it is often used to hide some defect, or to cheapen the colour by making insufficient grinding possible.

Powders must all be carefully sieved before they are despatched, otherwise particles not completely ground, together with gritty matter, will be found in the pigment, deteriorating its quality.
CHAPTER XIII.

MATCHING AND TESTING LAKE PIGMENTS.

The lake manufacturer is asked to match lakes, and, often, the only guide given him is a small piece of coloured paper or a painted slip. He has then to rely more upon his knowledge and experience of the pigments than upon any tests he can apply.

Where possible, a sample of the dry or pulp pigment should be obtained. Lakes in oil, varnish, and lithographic ink entail the trouble of removing the vehicle, and, in cases where the lake is soluble in the media, it is somewhat difficult to isolate the pigment unchanged.

When a centrifugal machine is not available, the oil can usually be readily separated from the pigment by adding, say, 5 c.c. carbon bisulphide to 15 gms. of the sample, stirring well, and diluting up with a mixture of 2 parts sulphuric ether and 1 of petroleum ether; wash by decantation twice, filter by means of a filter-pump, and wash on the filter paper with the mixed ethers until all the oil has been removed.

In cases where the only sample given is but a small piece of coloured paper, or dry painted surface, an experienced lake-maker can usually tell to what class of lakes it belongs, and, by referring to his own standards, can often devise a lake that will approximately give the colour required; but such a match must always be in a way unsatisfactory, for it is almost impossible, where the piece

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of paper has either been rolled, glazed, or varnished, to ascertain the actual shade of the untreated pigment. Where the sample supplied is a fair one, say an ounce or so, an assay of the colour is advisable. This can be readily carried out under the following scheme:

1. Examination of the colouring-matters.
2. Examination of the base.

*Examination of the Colouring-matters.* — There are many carefully thought-out processes for the identification of the various groups of colouring-matters, notably Green's Identification of Dyestuffs, which are of great interest scientifically, but take considerable time to apply, and this is not always at the disposal of the lake-maker. Until experience has been gained it is, however, necessary to rely upon these methods, and it is advisable starting with those colouring-matters that are frequently used in the colour-house, to make and have for personal reference standard lakes, and to retain samples of as many of the dyestuffs as possible.

When a colouring-matter has been identified, the conclusion may be verified by reference to a known lake made from the supposed colour or by reference to the dyestuff itself.

The examination of the colouring-matter may be carried out in the following manner:

Take a little of the pigment, rub it out with a little oil, put it on a glass plate, and note the shade and undertone. In single colour pigments it is often possible, after a little experience, to identify the colouring-matter by reference to these three points alone.

Reduce 1 of the pigment with 10 or 20 of zinc white, mixing thoroughly, and grinding well on a slate with a
muller, or, if only small quantities are being used, with a palette-knife on a glass plate.

Nearly all colours, as we have seen, differ in shade. The reduction in white accentuates these differences, and it may be taken as a safe conclusion that, if a pigment gives the same shade in oil and on reduction as one of the standard or known pigments, it is probably identical with it. The pigment should be treated in the cold with water, alcohol, benzene, turpentine, and white spirit, and its solubility in each of these noted. The mixtures of pigment and each of these solvents should then be boiled, and any increase or decrease in solubility also noted.

The sulphonic-acid azo pigments are insoluble, and the azo pigments soluble in benzene. This at once gives a key to the class should these colouring-matters be present.

Fastness to Bleeding.—If the pigment be for use as a pulp colour, rub out on paper in size; if as an oil colour, paint out on some surface, and allow to dry. Paint over the dry film a white in size in the case of a pulp, and in various media, such as gold size, or some vehicle let down with more or less quantities of alcohol, ether, white spirit or turpentine in the case of an oil colour, as the colouring-matter may be soluble in one or more of these, and would then bleed.

If the pigment does not bleed, then all bleeding colours of that shade are eliminated or vice versa.

Fastness to light is one of the most important points to determine. It is desirable to expose to sunlight in the presence of moisture, but, especially in winter, this cannot readily be done in this country, and the exposure cannot always be of the same duration. This difficulty can be surmounted, when time is important, by exposing painted-out films of pigment, in whatever vehicle is to be used.
to the ultra-violet rays of the mercury lamp, for six hours. This, though not equal to the sunlight exposure, gives a very good criterion of the fastness to light, an eosine being bleached in about two hours and a Helio Fast Red scarcely altered. The rate of fading under these conditions also gives a good indication of the nature, character, and class to which an unknown pigment belongs.

Several colours give very distinct colorations with strong sulphuric acid, and the behaviour of small quantities of the pigment with this reagent on a white plate, especially with reference to known or standard samples, is of help in finally determining the colouring-matter used.

Having noted the shade, the undertone, the strength by reduction, the solubility in various solvents, the fastness to light, and the behaviour with strong sulphuric acid, the following notes on the colour examination may be of use:—

Take a small portion of the pigment and rub it out evenly on a piece of paper with a little size or gum, to make it adhere, and dry at about 40° to 50° C. When dry, carefully compare the shade with the working standards, noting those colours and "makes" which most nearly approximate to it. Carefully feel the surface; if rough, a ground mineral base may be expected. Note the fulness, density, and brilliancy of the shade, since these properties, when considered in conjunction with the results yielded by an examination of the base, often suggest the manner in which the lake has been produced.

Cut off a portion of the coloured paper and heat it at 100° C., noticing whether the shade changes, or if there be any alteration in the pigment; for, as previously mentioned, if the colour be a maroon, changing a good deal at this temperature, it is to be inferred that the magenta is only combined with the acid colour, and therefore a match
will have to be so produced as to compete with it in price. In other cases, there may be evidence of some weakness, which has caused the user to look for another source of supply, and the matcher must then be on his guard to avoid this in his own product.

Divide the remaining piece of the paper, and spot one piece with a drop each of a 10 per cent. solution of strong nitric and hydrochloric acids. By reference to the valuable tables compiled by various authors, and with the help of indications previously obtained by comparison with lakes of known composition, determine the group to which the colour or colours belong, confirming the decision by further tests with the other slips, by spotting them respectively with caustic soda or potash, concentrated and dilute, and with acetic acid, strong and dilute.

The difficulty is not so much to identify the colour which has been used in the greatest quantity, but to determine those colours used to modify the shade.

Roughly classifying the lakes usually presented for matching, we shall find that a yellow lake will but rarely appear, since the chrome yellows are used, save for very special purposes, entirely to the exclusion of the yellow lake pigments. A chrome yellow can be so easily identified, and is so different from any yellow lake in its behaviour with reagents, that it would serve no useful purpose to enter into any details of its examination.

Yellow lakes prepared commercially are usually those of Naphthol Yellow S, Auramine, Thioflavine T, Quinoline Yellow, and Metanil Yellow, and examination of the standard shade would quickly show from which colour in all probability the lake was derived. Of the barium lakes

1 Georg Zeiss's tables are the most reliable.
there could be no mistake between those produced from Quinoline Yellow, Naphthol Yellow S, and Metanil Yellow, and the much greener hue of the Auramine basic lake would at once distinguish it from that obtained from Thioflavine T.

The addition of acids would further aid the detection:

Naphthol Yellow S—with hydrochloric acid, the colour almost disappears, and, with nitric acid, a reddish tone appears, which rapidly decolorizes.

Metanil Yellow—with hydrochloric acid, becomes much more red, and, with nitric acid, yields almost a scarlet.

Auramine O—with both hydrochloric and nitric acids is at once almost decolorized.

Quinoline Yellow—hydrochloric acid has very little action; with nitric acid becomes more red.

Thioflavine T is, like Auramine, at once decolorized by both hydrochloric and nitric acids, but, unlike auramine, when treated with caustic soda, becomes reddish instead of decolorizing.

The orange lakes are almost entirely derived from azo colours, and the various prices of these afford an indication as to which it will be necessary to use, when the price of the lake is known. All lake-makers have several standards of almost identical shades, but of very different prices, according to the nature of the lake pigment required. The behaviour of orange lakes with reagents is very similar, and the identification of any particular colour must, in the main, be determined by the brilliancy of the sample, the base with which it is thrown down, and the price limit. Frequently the lakes are mixtures of a cheap and a more expensive dyestuff, the cheaper colour being used to give intensity and fulness, the better one greater
brilliancy and fastness; and the colour-maker, for his own information, should keep a series of orange lakes of as great a variety of shades and costs as he can prepare, since it is only by such means that he is able to determine the constitution of an orange lake put before him. It may be advisable to mention here that the lakes made from Mandarin R and G, Orange II, and other cheap artificial orange colours are much inferior to the more expensive colours, such as the Brilliant Oranges of Meister Lucius & Brunning. Where time can be allowed, it is as well to expose to sunlight for two or three days a rubbing of the sample, for in many cases the degree of fading indicates fairly accurately the price of the colour used in its production.

Among the red, scarlet, and crimson lakes the question of determining the exact colour used in production of a given lake is rather more complicated, for it may belong to one of five classes, i.e.:—

I. Derived from Eosine.
II. Derived from Alizarine.
III. A developed azo colour.
IV. An ordinary lake of a sulphonated azo colour.
V. A red derived from some basic colour, such as Safranine, Magenta, etc.

An eosine lake is readily recognized after a little experience. The peculiar bright bloom and intensity of the colour leaves little room for doubt, and very short exposure to light—two or three hours in bright sunshine—will soon confirm such an idea, since the colour, if derived from an eosine, will then show signs of fading. The identification of a particular eosine is not a matter of such great ease, for nearly all eosine lakes are toned by the addition of various basic colours to give the required
shade, Rhodamines, Safranines, and Rose Bengal being those more generally used; Auramine is also used to give a yellow tone, but such a combination is of infrequent occurrence.

Eosines precipitated immediately, however, become yellow when treated with acids, and the colour in every case is readily dissolved out of the base on treatment with an alkali; even an alkaline salt, such as acetate of sodium, has this action, and the addition of a little alcohol generally causes the exhibition of considerable fluorescence.

Alizarine lakes change to yellow much more slowly with acids, and do not appear to be affected by dilute alkalies; further, their shade and appearance prevent them being mistaken for Ponceau lakes.

The Fast or Permanent Reds show but little change when treated with both dilute acids and dilute alkalies. This, together with their fastness to light, which is superior to that of all but alizarine lakes, gives a ready means of identifying them.

From the great number of Ponceau or Scarlet lakes, it is advisable for a lake-pigment maker to select a limited number, say nine, with whose properties and chemistry he has rendered himself thoroughly conversant, and to use these as his scarlets for the production of all lakes derived from this source. The use of a separate colour for each individual shade causes the number and variety of dyestuffs to accumulate rapidly, and it is therefore better to have a light medium and blue shade in three qualities of dyes—not three qualities of the same dye—and, in various stages of adulteration, to secure variety of price and properties. The lake-pigment maker will then be able, having once determined his standards, readily to match, at a given price, any lake pigment derived from this class, by
judicious admixture of the various scarlets at his command. If a special case arises, it is a simple matter to go carefully into the colouring-matter of such a lake, and to obtain a colour with the properties desired, if this is not already available.

Pure Magenta, Rhodamine, and Safranine lakes are readily identified by their characteristic shades, but are far more difficult to recognize when used in mixtures with other colours. Magenta is largely used with blue shades of Ponceau to produce maroon lakes; Safranines are also used for this purpose, but to a less extent, since their greater cost militates against them. Boiling a little of the lake with a solution of sodium carbonate, by dissolving the magenta or safranine, at once indicates the presence of either of these dyes, and, according to the depth and colour of the lake, the amount present can usually be readily gauged.

Rhodamines are used with eosine to give blue shades, this action on the colour affording a clue to their presence; and, on treatment with acid, a lake containing eosine and rhodamine does not become yellow so readily as the pure eosine.

Violet lakes, with the exception of those derived from Gallein, which become brown on treatment with acids, are for the most part derived from Methyl Violet, acid treatment of which changes the colour to blue. The shade is modified by the addition of Rhodamines, Magenta, etc., the proportion of which, and the colour to use, are best determined by comparison with lakes of known composition, since the complications arising from an endeavour to isolate the modifying colour in such mixtures makes the task one of considerable time and patience. This class of lakes is not used to any great extent, so that reference
to a series of modified violets will usually overcome any difficulty.

A large number of lakes are produced from the various basic blues. These lakes, however, differ but little from each other save in the redness of tone, and, to produce a complete series of shades that can be derived from the various basic blues, would be a task of considerable magnitude. It is therefore better to try to discover which blue has been used in the production of any particular shade. Those most commonly met with are Nile Blue, Methylene Blue, Basle Blue, New Blue, Water Blue, and Alkali Blue; and reference to such a table for the detection of artificial colouring-matters as that published by Lehne & Rusterholze, appearing in the Journal of the Society of Chemical Industry, vol. xiv., would quickly indicate the particular colouring-matter required to match a given sample.

The blues derived from allied alizarine colours are not met with in commerce to any great extent; those from such colours as the Erioglaucines and dyes of similar constitution are readily recognized by their pure shade, and extremely sensitive reaction to acids and alkalies.

Brown lakes form an unimportant class, and are mainly derived from Bismarck brown modified with other colours, the nature of which the shade indicates. The browner and deeper shades of maroon are often combinations of Bismarck Brown and a bluish-Ponceau. The Acid Browns are used to some extent, but the difference in the lakes produced by them is very great, and they are readily recognized as acid colours. The shade in nearly every instance indicates to the experienced lake-maker the brand of colour to be used.

Black lakes, excepting those for tinting purposes, are not much in demand, and, usually, one made from some
good black colouring-matter will meet requirements. Black lakes of a full deep colour are difficult to produce, the tendency being towards a deep navy-blue. Where a full deep black is met with, it is usually either a combination of logwood, or contains some black, like lamp, bone, or vegetable black.

The Examination of the Base.—The presence of some ground mineral can usually be detected by the "feel" of the lake when rubbed out on paper; but the following plan has been used with considerable success to determine roughly the constituents of a base. A small quantity of the dried lake is introduced into a porcelain crucible, and heated. In the case of arsenical colours the fumes of arsenic trioxide given off indicate, by their odour of garlic, the presence of arsenic. If the residue is almost entirely soluble in dilute acid, and aluminium hydrate is precipitated from the solution on the addition of ammonium hydrate, it may generally be concluded that the lake is an arsenical lake on a base of aluminium arsenite; if a phosphate, the precipitation of the phosphoric acid with ammonium molybdate shows the phosphate of aluminium to be in all probability present.

The colouring-matters are usually driven off or burnt by incineration in the crucible, the base or bases and the precipitating agent remaining. The presence of aluminium, iron, lead, or other inorganic matters can readily be detected by ordinary qualitative analysis. With a little practice, the insoluble residue can be identified without complete analysis, since it usually consists of either clay, barium sulphate, calcium sulphate, or mixtures of these. Calcium sulphate may be detected by adding a solution of sodium acetate and acetic acid to the ash: the calcium salts are taken up, and, after filtering and adding ammonium oxalate, are thrown down, calcium oxalate being
insoluble in acetic acid. Clay does not settle so readily as barium sulphate, but an intimate mixture of clay and precipitated barium sulphate is rather difficult to determine casually. Washing and drying the residue will enable the presence of clay to be determined, since it imparts a peculiar shiny appearance to the dried residue. Clay being an aluminium silicate, the silica can be driven off by treatment with hydrofluoric acid, and extraction with water will then leave only the sulphate of barium.

When ochres or other highly ferruginous compounds have been used as part of the base, the colour of the ash and the quantity of iron present indicates their use. If the quantity be not very excessive, but the presence of iron very distinctly indicated, the use of a brown, and not a white, barytes may be suspected.

Having determined the colouring-matters previously, a method to produce a match to the colour can easily be devised.

The following examples will perhaps illustrate the procedure better than more elaborate descriptions.

A sample of orange lake to be matched gave a smooth bright lake, intermediate in shade between those produced from Orange II and Mandarin R (Ber.). The lake, when incinerated, showed the presence of aluminium, a considerable amount of barium sulphate and some clay. A trial was made with—

56 parts clay.
100 ,, alum. sulph. 17 per cent.
35 ,, soda ash.
40 ,, Mandarin R.
20 ,, Orange II.
156 ,, barium chloride.

The shade produced was too red and too weak. The
clay was reduced to 28 parts, the Mandarin R to 30, and the Orange II increased to 30 parts; the shade was approximately that required, but a little too full. On increasing the clay to 35 parts, the lake produced matched the sample exactly.

Again, a maroon lake, much deeper in colour than any of the ordinary standards, rubbing out very smoothly, but deepening considerably on heating, gave a base similar to that described previously, but no possible combination with a blue shade of Ponceau, namely, Ponceau 4R (Ber.), gave the tone required. On heating the lake with a weak solution of sodium carbonate, a very dull, dirty magenta-coloured liquid was obtained. The addition of a brown colouring-matter, a proportion of Acid Brown B (Basle), to the Ponceau, gave a shade nearer to that required, but still not quite correct. By using a mixture of Bismarck brown and magenta the shade was finally determined.

A bright scarlet lake, the base of which proved to be a mixture of blanc-fixe and aluminium hydrate, was much more red than Ponceau GL (Ber.), much brighter than Scarlet GR, and much yellower than Scarlet 3R (M. L. & B.); but was matched by a mixture of Scarlet 3R, Ponceau GL, and Orange II, after two trials made to determine the correct quantities.
THE following short sketch of the combinations of the various hydrocarbons has been given, in order to illustrate how such combinations occur, to render the constitutional formulæ of the various colours more easily understood, and to enable the lake-maker to dissect the constitution of the colour, in order that he may not only apply the precipitating agent to the colour but convert it into a true lake. To enter into the theoretical consideration, and the modes of production of the various derivatives of the hydrocarbons of either the aromatic or fatty series, is beyond the scope of a text-book dealing with lake manufacture; for this, the reader is referred to some standard systematic work in organic chemistry.

In organic chemistry the compounds are divided into two series, the fatty and the aromatic, or the derivatives of methane and benzene respectively. It is from the latter the dyestuffs are derived, but radicles of the methane series enter into the combinations as well as inorganic radicles, such as amido, hydroxy, azo, and sulphonic-acid groups.

The carbon compounds of the methane series are the derivatives of a homologous series of hydrocarbons of which the simplest member is methane $\text{CH}_4$; and by the substitution of one of the hydrogen atoms in the latter by the methyl-radicle, a series of compounds of increasing complexity is derived.
The Manufacture of Lake Pigments.

\[
\begin{align*}
\text{Methane.} & \quad C^\cdot \begin{cases} H \\ H \\ H \\ H \end{cases} \\
\text{Ethane.} & \quad C^\cdot \begin{cases} H \\ H \\ \text{CH}_3 \end{cases}
\end{align*}
\]

As the number of methyl-radicles increases, substitution can take place in more than one grouping, giving rise to isomers; e.g., there are five isomers of hexane, namely—

Normal hexane, \( \text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3 \)

Isohexane, \( \text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH} \left\{ \begin{cases} \text{CH}_3 \\ \text{CH}_3 \end{cases} \right\} \)

Tetramethyl-ethane, \( \text{CH}_3\cdot\text{CH}_3\cdot\text{HC—CH} \left\{ \begin{cases} \text{CH}_3 \\ \text{CH}_3 \end{cases} \right\} \)

Methyldiethyl-methane, \( \text{CH}_3\cdot\text{CH}\left\{ \begin{cases} \text{CH}_2\cdot\text{CH}_3 \\ \text{CH}_3 \end{cases} \right\} \)

Trimethylethyl-methane, \( \text{H}_3\text{C—C—CH}_2\cdot\text{CH}_3 \)

In colouring-matters these hydrocarbons and their compounds are chiefly met with as substituent groupings for hydrogen or some radicle, and the most important compounds of these hydrocarbons, simple and complex, may be roughly classified as—

The ethers or oxides of the radicle, such as ethyl ether \( \text{C}_2\text{H}_5\cdot\text{O} \)

or for the whole series, letting \( R \) represent the radicle \( \text{R—O} \).

The alcohols or hydroxides, for example, ethyl alcohol, \( \text{C}_2\text{H}_5\cdot\text{OH} \), or \( \text{R—OH} \).

The acids; acetic acid may illustrate \( \text{CH}_3\cdot\text{C—O—OH} \) or \( \text{R—COOH} \). The aldehydes; the partially oxidized alcohols, for instance, acetic aldehyde, \( \text{CH}_3\cdot\text{C—O} \) or \( \text{R—C—H} \).

The ketones; oxidized secondary alcohols, e.g., acetone

\[ \begin{cases} \text{CH}_3 \\
\text{CH}_3 \end{cases} \cdot \text{CO}, \quad \text{or} \quad \begin{cases} \text{R} \\ \text{R} \end{cases} \cdot \text{CO} \]
These simple illustrations may be taken as representative of the classes into which the compounds of the methyl series may be divided; but it must be borne in mind that the substitution products and the derivatives of the higher members of the hydrocarbons form much more complex bodies than those outlined above. Glycerine is an alcohol of this series, but it is a trihydroxy body, \( C_3H_8(OH)_3 \).

Oxalic and succinic acids are examples of more complex acids. Oxalic acid may be looked upon as acetic acid, in which the methyl-radicle has been oxidized to the carboxyl group—

\[
\begin{align*}
\text{CH}_3 & \quad \text{C} : \text{O} \cdot \text{O} \cdot \text{H} \\
\text{C} : \text{O} \cdot \text{H}, & \quad \text{C} : \text{O} \cdot \text{O} \cdot \text{H} \\
\text{Acetic acid} & \quad \text{Oxalic acid}
\end{align*}
\]

Succinic acid, \( C_2H_4(COOH)_2 \). The acids of this series have the general formula \( R(COOH)_2 \).

The simplest representative of the aromatic or benzene series is benzene, \( C_6H_6 \), which is assumed to be represented by six carbon atoms combined to form a ring, each carbon atom being also combined with a hydrogen atom. Thus—

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} \\
\text{C} & \quad \text{C} = \quad \text{C} \\
\text{C} & \quad \text{C} = \quad \text{C} \\
\text{H} & \quad \text{H} & \quad \text{H}
\end{align*}
\]

or more simply by \( \text{[\text{ring}] \quad \text{[\text{ring}]} } \); but the sign \( \text{[\text{ring}] \quad \text{[\text{ring}]} } \), as a general rule, represents this hydrocarbon.

The homologues of this series are formed by the substitution of the hydrogen, combined with one of the carbon atoms, by the methyl-radicle, e.g., toluene \( \text{[\text{ring}]} \), xylene \( \text{[\text{ring}] \quad \text{CH}_3} \).
Reference to the formula of benzene will show, however, that, in xylene, the methyl-radicle (CH$_3$), can be substituted in the benzene ring, in three different positions with respect to each other. Without entering into a detailed account of the theory of this question, it is sufficient to note that the properties of a disubstitution product of benzene vary considerably, according to the position of the second substituent grouping.

The three positions have been named the ortho-, meta-, and para-positions.

The ortho-position is that in which the hydrogens are substituted in two adjacent carbon atoms in the benzene ring,

\[ \text{e.g., ortho-xylene} \]

The meta-position. The hydrogens substituted are separated by one intervening unsubstituted hydrogen; metaxylene

\[ \text{meta-xylene} \]

The para-position. Two unsubstituted hydrogens intervene between the substituted hydrogens; paraxylene

\[ \text{para-xylene} \]

Naphthalene, C$_{10}$H$_8$, may be regarded as a condensation product of two benzene rings.

Thus—

\[
\begin{align*}
\text{Benzene} & \quad \text{Benzene} & \quad \text{Naphthalene} \\
8 & \quad 1 & \quad 8 \\
7 & \quad 2 & \quad 5 \\
6 & \quad 3 & \quad 6 \\
5 & \quad 4 & \quad 3 \\
4 & \quad 5 & \quad 4 \\
3 & \quad 6 & \quad 5 \\
2 & \quad 7 & \quad 2 \\
1 & \quad 8 & \quad 1 \\
0 & \quad 9 & \quad 0
\end{align*}
\]

written generally

It will be seen that there are eight
hydrogen atoms in this hydrocarbon, in which substitution can take place. An examination of the formula shows that the hydrogen atoms may be divided into two groups, namely, $1:4:5:8$ and $2:3:6:7$. The several members of each group bear the same relations to each other, but differ from the members of the other group; for $1:4:5:8$ are linked to carbon atoms which are not combined with hydrogen, and $2:3:6:7$ are linked as in an ordinary benzene ring. From this it can easily be surmised that, of the isomeric mono-substitution products of naphthalene, two classes are known and have been isolated, viz., $\alpha$ and $\beta$ substitution products. The alpha-substitution products are those in which the hydrogen in $1:4:5$ or $8$ is substituted, and the beta those in which the hydrogen in either $2:3:6$ or $7$ has been replaced—

\[
\begin{align*}
\text{Naphthalene disulphonic acid (2:6)} & \begin{array}{c}
\text{SO}_2H \\
\text{HO}_2S
\end{array} \\
\text{Naphthalene disulphonic acid (2:7)} & \begin{array}{c}
\text{SO}_2H \\
\text{HO}_2S
\end{array}
\end{align*}
\]

In like manner, anthracene, $C_{14}H_{10}$, may be considered as a condensation product of three benzene rings—

\[
\begin{align*}
\text{Benzene. Benzene. Benzene.}
\end{align*}
\]

\[
\begin{align*}
\text{Anthracene.}
\end{align*}
\]
This hydrocarbon is used almost entirely for the production of alizarine colours, and, since these have almost exclusively one general formation, it will not be of service to enter into the reactions of anthracene.

The derivatives of benzene and naphthalene occur widely in combination with chromophors in colouring-matters, and, besides playing an important part in the colour molecule, it is chiefly to their reactions, and their influence that the lake-forming properties of the colours are due. It is therefore essential to survey briefly the more important derivatives.

The monohydroxy derivatives: those in which one hydrogen atom of the hydrocarbon has been substituted by the hydroxy-radicle, (OH), which confers weak acid properties. The principal members of this group are—

\[
\begin{align*}
\text{Phenol or carbolic acid} & \quad \text{OH} \\
\text{Ortho- meta- and para-cresol} & \quad \begin{array}{c}
\text{o, CH}_3 \\
\text{m, CH}_3 \\
\text{p, CH}_3
\end{array} \\
\text{Alpha- and beta-naphthol} & \quad \begin{array}{c}
\text{a, OH} \\
\text{b, OH}
\end{array}
\end{align*}
\]

The primary amines: hydrocarbons in which one hydrogen atom has been replaced by the amido-radicle, (NH\(_2\)), giving a distinctly basic nature to the compound, and causing it to combine readily with acids. Amido compounds when acted upon with nitrous acid (HNO\(_2\)) are converted into diazo compounds, \(\text{e.g.} \) —

\[
\text{R·NH}_2\text{HCl + HNO}_2; \text{R·N: NCl + 2H}_2\text{O}
\]
Of this group the more important members are—

\[
\text{NH}_2
\]

\text{Aniline}

The ortho- meta- and para-toluidines—

\[
\begin{align*}
\text{o, CH}_2 \text{NH}_2 & \\
\text{m, CH}_3 \text{NH}_2 & \\
\text{p, CH}_3 \text{NH}_2 & 
\end{align*}
\]

The xyldenes, amido-m.-xylene—

\[
\begin{align*}
\text{CH}_3 & \\
\text{CH}_3 & \\
\text{NH}_2 & \\
\text{amido-p.-xylene} & , \\
\text{CH}_3 & \\
\text{CH}_3 & \\
\text{NH}_2 & 
\end{align*}
\]

Cumidine, and

\[
\begin{align*}
\text{H}_2\text{N} & \\
\text{CH}_3 & \\
\text{CH}_3 & \\
\text{a, NH}_2 & \\
\text{b, NH}_2 & 
\end{align*}
\]

Alpha- and beta-naphthylamine

The sulphonic acids are those substitution products in which one or more hydrogen atoms have been replaced by the radicle \((\text{HSO}_3)\); this gives distinctly acid properties, and the sulphonic acids readily combine with basic oxides, in many cases producing insoluble compounds.

The chief members of this group are—

Benzene monosulphonic acid, \(\text{C}_6\text{H}_5\text{SO}_3\text{H}\)

Meta- and para-benzene disulphonic acids

Alpha- and beta-naphthalene monosulphonic acids
The naphthalene disulphonic acids, which are in some cases distinguished by the names of the discoverers—

Armstrong's δ-acid (1 : 5)

Ewer and Pick's acid (1 : 6)

Armstrong's γ-acid (1 : 7)

Ebert and Merz's β-acid (2 : 6)

The tri- and tetra-naphthalene sulphonic acids, C_{10}H_{5}(SO_{3}H)_{3}, C_{10}H_{4}(SO_{3}H)_{4}.

The Organic Acids.—The carboxyl or acid-forming radicle gives, with the hydrocarbons, true acids. It has been shown that the oxidation of ethane results in the formation of acetic acid, CH_{3}COOH, which may be regarded as methane, in which one of the hydrogens is substituted by the carboxyl-radicle, (COOH). Thus the substitution of hydrogen atoms in the aromatic hydrocarbons gives rise to distinct acids, of which the following are of most interest:—

COOH

Benzoic acid, \[ \text{COOH} \]

Phthalic acid, orthobenzene dicarboxylic acid, \[ \text{COOH} \]

and its di- and tetra-halogen derivatives, C_{6}H_{2}Cl_{2}COOH, C_{6}Cl_{4}COOH.
The Nitro Compounds.—These are formed from the hydrocarbons by the substitution of the nitro-radicle \((\text{NO}_2)\), for one or more hydrogen atoms, such substitution imparting acid properties to the compounds. The leading members of this series are:

\[
\text{Nitrobenzene, } C_6H_5\text{NO}_2
\]

\[
m.-\text{dinitrobenzene, } C_6H_4(\text{NO}_2)_2
\]

\[
o.- \text{ and p.-nitrotoluene, } C_6H_4\text{CH}_3\text{NO}_2
\]

\[
\text{Dinitrotoluene, } C_6H_4\text{CH}_3(\text{NO}_2)_2 \quad 1:2:4
\]

\[
\text{Nitroxylol, } C_6H_3(\text{CH}_3)_2\text{NO}_2 \quad 1:2:4
\]

\[
\alpha-\text{nitrornaphthalene, } C_{10}H_7\text{NO}_2
\]

\[
\alpha-\text{dinitronaphthalene, } C_{10}H_6\text{NO}_2
\]

The substitution products dealt with above have been chiefly the monosubstitution bodies, but substitution can take place in more than one position at the same time, and in the same molecule. Of the multisubstitution products in which the hydroxy-radicle occurs, the chief are:

\[
\text{Resorcinol, } C_6H_4(\text{OH})_2
\]
Orcinol, \( C_6H_3(CH_3)\cdot((OH)_2) \cdot \)

Pyrogallol, \( C_6H_3(OH)_3 \)

The dioxy-naphthols, of which there are ten, \( C_{10}H_6(OH)_2 \):

\[ \text{e.g.} \]

Among the amido multi-substitution products are found the diamines, and the secondary and tertiary amines. Of the diamines the principal members are:

The phenylene diamines, \( C_6H_4(NH_2)_2 \)

The tolylene diamines, \( C_6H_4CH_3(NH_2)_2 \)

\( (1 : 2 : 4) \quad NH_2 (1 : 2 : 5) \quad NH_2 \quad NH_2 \quad NH_2 \quad NH_2 \)

With this class, the diamines in which substitution has already taken place in the amido-radical may be considered; \textit{e.g.}—

Diphenyl m.-phenylenediamine, \( C_6H_4NHC_6H_5 \)

Diphenyl naphthylenediamine, \( C_{10}H_6NH\cdotC_6H_5 \)

Diamido-diphenylamine, \( NH(C_6H_4NH_2)_2 \)

Benzidine, \( C_6H_4NH_2 \)

Toluidine, \( C_6H_3CH_3NH_2 \)
Among the secondary and tertiary amido-derivatives are found—

Diphenylamine, $\text{NH}_2\left(\text{C}_6\text{H}_5\right)\left(\text{C}_6\text{H}_5\right)$

Benzylaniline, $\text{C}_6\text{H}_5\text{NH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_5$,

Dimethylaniline, $\text{N} - \text{CH}_3$

Dimethyl-a-naphthylamine, $\text{C}_{10}\text{H}_7\text{N}(\text{CH}_3)_2$

Phenyl-a-naphthylamine, $\text{C}_{10}\text{H}_7\text{NH}\text{C}_6\text{H}_5$

Quinoline, $\text{C}_9\text{H}_7\text{N}$

Quinaldine, $\text{C}_{10}\text{H}_9\text{N}$

Carbazol, $\text{C}_{12}\text{H}_9\text{N}$

Orthomethyl benzidine,

$\text{C}_6\text{H}_4\text{NH}_2(1:4)$, $\text{C}_6\text{H}_3(\text{CH}_3)\text{NH}_2(1:3:4)\text{H}_2\text{N}$

Diamido carbazol, $\text{HN}$

p.-diamido stilbene, $\text{C}_6\text{H}_4(\text{NH}_2)\text{CH} : \text{CH} \cdot \text{C}_6\text{H}_4\text{NH}_2$
The sulphonic acids of the amido- and hydroxy-derivatives are of the utmost importance, being of frequent occurrence in the molecules of colouring-matters. The chief phenol-sulphonic acids are—

\[
\text{o. and p.-phenol sulphonic acid, } C_6H_4SO_3\text{HOH}
\]

The \( \alpha \)-naphthol monosulphonic acids, \( C_{10}H_8\text{SO}_3^+ \), of which there are several isomers, but the most important is a naphthol monosulphonic acid, NW, \( 1:4 \)

\[
\text{The } \alpha \text{-naphthol disulphonic acids, } C_{10}H_8(\text{HSO}_3)_2, \text{ of which of the many isomers (1:2:4)}
\]

\[
\text{and (1:2:7) are the principal}
\]

\[
\text{The } \alpha \text{-naphthol trisulphonic acids, of which the following two are the most common:—}
\]

\[
\text{a-naphthol trisulphonic acid, } 1:2:4:7
\]

\[
\text{a-naphthol trisulphonic acid, } 1:3:6:8
\]

The \( \beta \)-naphthol monosulphonic acids, four of which are generally in use, namely—

\[
\text{Bayer's acid, } C_{10}H_8\text{SO}_3^+(2:8)
\]

\[
\text{Schaffer's acid, } C_{10}H_8\text{SO}_3^+(2:6)
\]
Dahl's acid, $C_{10}H_6SO_3H(2:5)$

Cassella's acid, $C_{10}H_6SO_3H(2:7)$

The $\beta$-naphthol disulphonic acids. Of the many isomers, the following are of most importance—

$\beta$-naphthol disulphonic acid, $C_{10}H_5OH(SO_3H)_{2}(2:3:6)$

$\beta$-naphthol disulphonic acid, $C_{10}H_5OH(SO_3H)_{2}(2:6:8)$

$\beta$-naphthol trisulphonic acid, $C_{10}H_4OH(SO_3H)_3$, most probably $2:3:6:8$

The sulphonic acids of the dioxynaphthalenes are important derivatives of this group, and give rise to many isomers; those in use are believed to be various mixtures whose exact constitutions are unknown.

The amido-sulphonic acids are of equal importance with the hydroxy-sulphonic acids. The principal members of use in lake manufacture are—

The sulphanilic acids, $C_6H_4NH_2SO_3H$

Phenylhydrazine p.-sulphonic acid, $C_6H_4NNH_2SO_3H$

The toluidine sulphonic acids, $C_6H_2(CH_3)(NH_2)SO_3H$

The xylidine sulphonic acids, $C_6H_2(CH_3)_2(NH_2)SO_3H$
The α-naphthylamine sulphonics, \( C_{10}H_7NH_2SO_3H \), of the seven isomers of which \((1:4), (1:3), (1:6), (1:8), \) and \((1:2)\) occur most frequently in colour molecules. α-naphthylamine sulphonics acid

\[
\begin{align*}
1:4 & \quad \text{etc.} \\
1:6 & \\
\end{align*}
\]

The α-naphthylamine disulphonic acids and trisulphonic acids. The following of the many isomers will serve to illustrate their constitution—

α-naphthylamine disulphonic acid, \( C_{10}H_8NH_2(SO_3H)_2 \)

\[
\begin{align*}
(1:3:8) & \\
\end{align*}
\]

α-naphthylamine trisulphonic acid, \( C_{10}H_8NH_2(SO_3H)_3 \)

\[
\begin{align*}
(1:2:4:7) & \\
\end{align*}
\]

The β-naphthylamine mono-, di-, and trisulphonic acids are equally important with those of α-naphthylamine, and their constitution is similar, save that the amido group is in the β-position.

Referring to the sulphonic acids of the diamines, and the secondary and tertiary amines, the following are of importance:—

Methyl and ethyl β-naphthylamine sulphonics acid, \( C_{10}H_6SO_3HNHCH_3 \) and \( C_{10}H_6SO_3HNHCH_2CH_3 \)

Diamido-naphthalene disulphonic acids, \( C_{15}H_4(NH_2)_2(SO_3H)_2 \)

\[
\begin{align*}
1:5:3:7 & \quad \text{and (1:8:3:6)} \\
\end{align*}
\]
The amido-phenols, that is, those compounds in which both the hydroxy- and the amido-radicles occur, may be illustrated by—

\[ m\text{-Amido-phenol, } C_6H_4NH_2OH \]

and derivatives such as dimethyl-amido-phenol, \( C_6H_4\left(\text{N(CH}_3\text{)}_2\right)\text{OH} \), and diethyl-amido-phenol, \( C_6H_4\left(\text{N(C}_2\text{H}_5\text{)}_2\right)\text{NO} \), from which are derived nitroso compounds similar to \( C_6H_3\text{NO} \) and \( C_6H_3\left(\text{N(CH}_3\text{)}_2\right)\text{NH} \).

Of the amido-naphthols several are largely used in the preparation of azo colours. A type may be expressed in this manner:

\[ C_{10}H_5\text{OHNNH}_2(1:2) \]

The amido-naphthols give rise to a series of mono-, di-, and trisulphonic acids, which are of great importance in the production of the above-mentioned azo-colours. There are many isomers; they may be written thus:

The monosulphonic acids, \( C_{10}H_5\text{NH}_2\text{OHSO}_3\text{H}(2:3:7) \)

The disulphonic acids, \( C_{10}H_5\text{NH}_2\text{OH(SO}_3\text{H)}_2(2:3:6:8) \)

Among the derivatives of the amido-phenols may be counted anisidine, the methyl ether of amido-phenol,
and dianisidine,

\[
\begin{align*}
C_6H_3(OCH_3)NH_2 \\
C_6H_3(OCH_3)NH_2
\end{align*}
\]

The amido-nitro compounds are of considerable importance:

The nitranilines, \( C_6H_4NH_2NO_2 \),

The nitrotoluidines, \( C_7H_8NH_2NO_2 \),

Of the multisubstitution products containing the carboxyl-radicle, \( COOH \), and its derivatives, the following are some of the best examples:

Amido-benzoic acid, \( C_6H_4NH_2COOH \)

Salicylic acid, \( C_6H_4(OH)COOH \)

Amido-salicylic acid, \( C_6H_3(OH)(NH_2)COOH \)

Cresolic acids, \( C_6H_3(CH_3)(OH)COOH \)

Gallic acid, trioxybenzoic acid, \( C_6H_2(OH)_3COOH \)

\( \alpha \)-naphthol carboxylic acid, 

The introduction of the oxidation products of the fatty hydrocarbons, the aldehydes, ketones, etc., gives rise to a series of compounds, of which those of the greatest importance are:
Benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$, and its derivatives, mono-
and dichlorbenzaldehyde, $\text{C}_6\text{H}_4\text{ClCHO}$

The following hydroxy, nitro, and amido derivatives are of considerable interest:—

The nitro-benzaldehydes, $\text{C}_6\text{H}_4(\text{NO}_2)\text{CHO}$

The amidó-benzaldehydes, $\text{C}_6\text{H}_4(\text{NH}_2)\text{CHO}$

The oxybenzaldehydes, $\text{C}_6\text{H}_4(\text{OH})\text{CHO}$

Of the ketones $\text{R} - \text{C} - \text{R}$, the following are of interest:—

Benzophenone, $\text{C}_6\text{H}_5\cdot\text{C} - \text{O} - \text{C}_6\text{H}_5$, and its derivatives the Amido-benzo phenones, $\text{C}_6\text{H}_5\cdot\text{C} - \text{O} - \text{C}_6\text{H}_4\text{NH}_2$

The diamido-benzo phenones, $\text{C}_6\text{H}_4\text{NH}_2\cdot\text{C} - \text{O} - \text{C}_6\text{H}_4\text{NH}_2$

The oxidation of anthracene, $\text{C}_{14}\text{H}_{10}$ gives rise to anthraquinone from which alizarine colours are derived.
Anthraquinone, $C_{12}H_5(CO)_2$ or

\[ C_6H_4\begin{array}{c} CO \\ CO \end{array}C_6H_4 \]

THE END.
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