MANUFACTURE OF LAKE PIGMENTS FROM ARTIFICIAL COLOURS

F. H. JENNISON

THE

MANUFACTURE OF LAKE PIGMENTS

FROM

ARTIFICIAL COLOURS

THE
MANUFACTURE OF LAKE PIGMENTS
FROM
ARTIFICIAL COLOURS

BY

FRANCIS H. JENNISON, F.I.C., F.C.S.

WITH SIXTEEN PLATES
SHOWING SPECIMENS OF EIGHTY-NINE COLOURS

LONDON
SCOTT, GREENWOOD & SON
THE OIL AND COLOUR TRADES JOURNAL," OFFICES
8 BROADWAY, LUDGATE HILL, E.C.

CANADA: THE COPP CLARK CO. LTD., TORONTO
UNITED STATES: D. VAN NOSTRAND CO., NEW YORK
1900

CONTENTS

THE
MANUFACTURE OF LAKE PIGMENTS FROM ARTIFICIAL COLOURS

CHAPTER I

INTRODUCTION

The term "lake colour" is used to distinguish pigments made from dyestuffs and colouring matters, by precipitating the colouring matter as an insoluble compound, which can then be used for pigmental purposes, to distinguish them 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.

Until 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 which are still in the market, and known by such names as crimson lake, berry yellow, madder lake, Dutch pink, rose lake, leather lake, etc.; but of recent years they have, but for some few and particular purposes, been superseded by lakes made from artificial colours, because the latter can be produced more easily and cheaply, and possess greater staining power, brilliancy, and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.

To manufacture lakes from artificial dyestuffs, in order to produce the best and most economical results, to adapt the lake to the purpose for which it is required, it is necessary to understand the chemistry, constitution, and properties of the colours used.

The difficult and intricate chemistry of the production of the artificial dyestuffs does not concern the lake manufacturer, but the chemical nature of the colour he is using does; *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, but rather the substitution and addition products of the chromophor. For instance—

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

$$HSO_3—C_6H_4N : N—C_6H_4NH_4C_6H_5$$

$$\text{or } C_6H_4 \begin{cases} SO_3H \\ N : N\cdot C_6H_4NHC_6H_5 \end{cases}$$

The chromophor of this colour is azo-benzene—

$$C_6H_5\cdot N : N\cdot C_6H_5$$

Examining the formula of the colour, 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 radicals.

The sulphonic acid rendering the colour of an acid nature, by virtue of which it is used as a dye, is the group that has to be considered when it is attempted to form a lake from this colouring matter.

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. Kelonimides and hydrazides.
VI. Tripheylamine colours.
VII. Azines, oxazines, and thioazines.
VIII. Quinoline colours.
IX. Acridine 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 radicals 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 radical is a group of atoms which go through a series of compounds without alteration, and 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, *e.g.*, the methyl-radical, CH_3, which when combined with hydrogen forms methane, CH_4, which when treated with iodine gives iodo-methane, $CH_4 + I = CH_3I + HI$. Acting on iodo-methane with sodium, we get ethane, $2CH_3I + Na_2 = 2NaI + \left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right.$; this hydrocarbon when treated with iodine forms iodo-ethane, C_2H_5I; on the addition of ammonia, iodo-ethane forms ethylamine, $C_2H_5I + NH_3 = C_6H_5NH_2 + HI$; when ethylamine is combined with nitrous acid it forms ethylamine nitrite, which when heated yields $C_6H_5NH_3NO_2 = N_2 + H_2O + \underset{\text{Alcohol.}}{C_2H_5OH}$. When alcohol is oxidised it gives acetic acid, CH_3COOH, the sodium salt of which, when treated with caustic soda, yields methane. Thus, $CH_3COONa + NaOH = CH_4 + Na_2CO_3$, showing that after many changes the radical, CH_3, has passed through them without alteration.

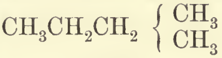
In organic chemistry the compounds are divided into two series, the fatty and the aromatic, or the derivatives of methyl and benzene; it is from the latter that the dyestuffs are derived, but the radicals of the methyl series enter into the combinations as well as inorganic radicals, such as amido, hydroxy, and azo groups.

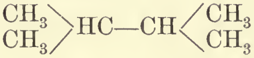
The carbon compounds of the methyl series are the derivatives of a homologous series of hydrocarbons, of which the simplest member is methane, CH_4, from which a series of compounds of increasing complexity is derived by the substitution of one of the hydrogens in the methane by the methyl-radical. For instance—

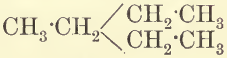
$$\underset{\text{Methane.}}{C\left\{\begin{matrix}H\\H\\H\\H\end{matrix}\right.} \qquad \underset{\text{Ethane.}}{C\left\{\begin{matrix}H\\H\\H\\CH_3\end{matrix}\right.}$$

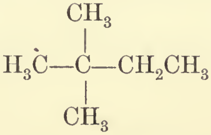
As the number of methyl-radicals increase, substitution can take place in any one, and this gives rise to isomers in the more complex groups; *e.g.*, hexane gives rise to five, namely—

Normal hexane, $CH_3{\cdot}CH_2CH_2CH_2CH_3$

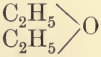
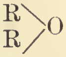
Isohexane, 
$CH_3CH_2CH_2\left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right.$

Tetramethyl-ethane, 

Methyldiethyl-methane, 

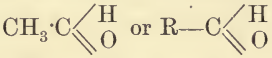
Trimethylethyl-methane, 
$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_2CH_3$

In colouring matters these hydrocarbons and their compounds are mainly met with as substitutes for hydrogen or some radical, and the main classes of the compounds of these hydrocarbons, simple and complex, may be roughly classified as—

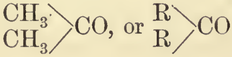
The ethers or oxides of the radical, such as ethyl ether 
or for the whole series, letting R represent the radical 

The alcohols or hydroxides, for example, ethyl alcohol, C_2H_5OH, or R—OH.

The acids; acetic acid may illustrate $CH_3{\cdot}C : O{\cdot}OH{\cdot}R{\cdot}COOH$.

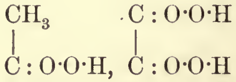
The aldehydes; the partially oxidised alcohols, for instance, acetic aldehyde, 

The ketones, or the oxidised acid, as acetone, shows



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; for instance, glycerine is an alcohol of this series, but is a trihydroxy alcohol, $C_3H_5(OH)_3$.

Oxalic and succinic acids may be instanced as more complex acids. Oxalic acid may be looked upon as acetic acid, in which the methyl-radical has been oxidised to the carboxyl group—

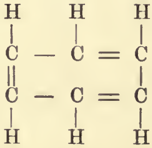


$$\begin{array}{cc} CH_3 & C:O\cdot O\cdot H \\ | & | \\ C:O\cdot O\cdot H, & C:O\cdot O\cdot H \end{array}$$

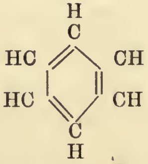
Acetic acid. Oxalic acid.

Succinic acid, $C_2H_4(COOH)_2$. The acids of this series may be indicated therefore by $R(COOH)_2$

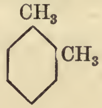
The simplest representative of the aromatic or benzene series is benzene, C_6H_6, which is assumed to be represented by six carbon atoms combined in a ring, each carbon atom being also combined with a hydrogen atom. Thus—



; or, as usually written,



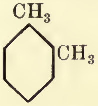
or more simply by , but the sign , as a general rule, represents the hydrocarbon-benzene.

The homologues of this series are formed by the substitution of the hydrogen, combined with one of the carbon atoms, by the methyl-radical, *e.g.*, toluene , xylene 

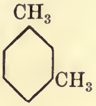
Reference to the formula of benzene will show, however, that in xylene the methyl-radical, (CH_3), can be substituted in the benzene ring, in three different positions in relation to each other, without entering into a detailed account of the theory of this question, it being sufficient to note that the properties of a disubstitution product of benzene differ considerably, as the position of the substituting body or bodies varies.

These 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, *e.g.*, ortho-xylene



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



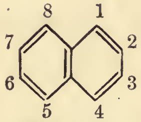
The para-position. Two unsubstituted hydrogens intervene between the substituted hydrogens, paraxylene

Naphthalene, $C_{10}H_8$, may be regarded as a condensation of two benzene rings.

Thus—

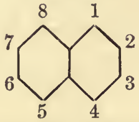
Benzene.

Benzene.



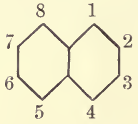
Naphthalene.

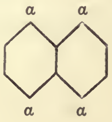
generally written

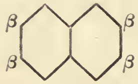


It will be seen that there are eight hydrogen atoms in this hydrocarbon, in which substitution can take place. An examination of the formula will show that these hydrogens may be divided into two groups, namely, 1 : 4 : 5 : 8 and 2 : 3 : 6 : 7. The several members of each group bear the same relations 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 these isomeric monosubstitution products of naphthalene, two classes are known and have been isolated, and are known as the α and β 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 have been replaced—

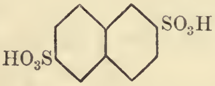






The multisubstitution products give rise to many isomers, but it is usual to indicate the position when known by the numerals. Thus—

Naphthalene disulphonic acid (2 : 6)



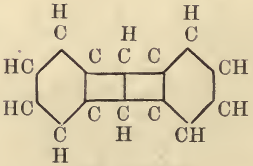
Naphthalene disulphonic acid (2 : 7)

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


Benzene.


Benzene.


Benzene.



Anthracene.

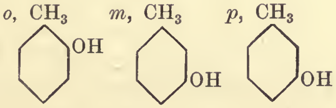
This hydrocarbon is used almost entirely for the production of alizarine colours, and, as these have almost exclusively one general formation, it will not be of service to enter into the reactions of anthracene, as, from a lake-producing point of view, it would have but little value, and it does not occur in any form in by far the greater number of colours, in combination with various radicals or by itself. The derivatives of benzene and naphthalene occur largely in combination with chromophors in colouring matters, and, besides playing an important part in the colour molecule, their reactions, and their influence on the nature of the colours, form the chief means by which lakes are formed. It is therefore essential to briefly survey the more important derivatives.

The monohydroxy derivatives, *i.e.*, those in which the hydrogen of the hydrocarbon has been substituted by the hydroxy-radical, (OH).

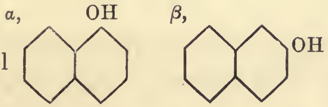
This radical, (OH), has the property of imparting weak acid properties to the hydrocarbons, and the principal members of this group are—

Phenol or carbolic acid

Ortho- meta- and para-cresol



Alpha- and beta-naphthol



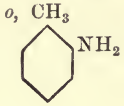
The primary amines, in which the hydrogen is substituted by the amido-radical, (NH_2), giving a distinctly basic nature to the compound, thus causing it to readily combine with acids. Amido compounds when acted upon with nitrous acid (HNO_2) are converted into diazo compounds, *e.g.*—

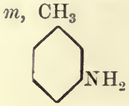
$$R\cdot NH_2HCl + HNO_2 ; \; R\cdot N : NCl + 2H_2O$$

Of this group the more important members are—

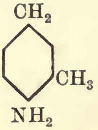
Aniline

The ortho- meta- and para-toluidines—

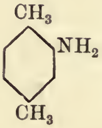




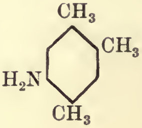
The xylidenes, amido-m.-xylene—



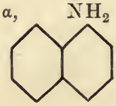
amido-p.-xylene

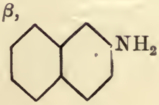


Cumidine



Alpha- and beta-naphthylamine





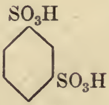
The sulphonic acids are those substitution products in which the hydrogen has been substituted for the radical (HSO_3); this gives distinctly acid properties, and the sulphonic acids readily combine with basic oxides, and in many cases producing insoluble compounds.

The chief members of this group are—

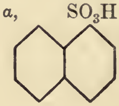
SO_3H

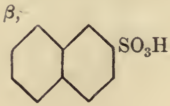
Benzene monosulphonic acid, $C_6H_5SO_3H$

Meta- and para-benzene disulphonic acids



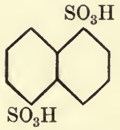
Alpha- and beta-naphthalene monosulphonic acids



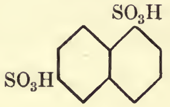


The naphthalene disulphonic acids, which are in some cases distinguished by the names of the discoverers—

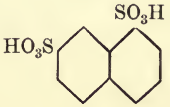
Armstrong's δ-acid (1 : 5)



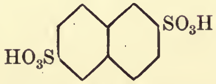
Ewer and Pick's acid (1 : 6)



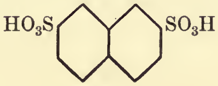
Armstrong's γ-acid (1 : 7)



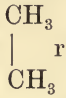
Ebert and Merz's β-acid (2 : 6)



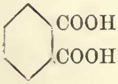
" " α-acid (2 : 7)



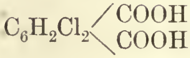
The tri- and tetra-naphthalene sulphonic acids, $C_{10}H_5(SO_3H)_3$, $C_{10}H_4(SO_3H)_4$.

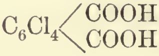
The carboxyl or acid-forming radical. This group forms, with the hydrocarbons, true acid, and as it has been shown that the oxidation of ethane  $\begin{array}{c}CH_3\\|\\CH_3\end{array}$ results in the formation of acetic acid, CH_3COOH, which practically is methane, in which one of the hydrogens is substituted by the carboxyl-radical, (COOH), so the substitution of the hydrogen in the aromatic hydrocarbons gives rise to distinct acids, of which the following are of most interest:—

Benzoic acid,

Phthalic acid, orthobenzene dicarboxylic acid, 

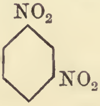
and

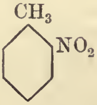
its di- and tetra-halogen derivatives, 
$C_6H_2Cl_2\left\langle\begin{matrix}COOH\\COOH\end{matrix}\right.$

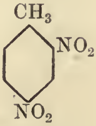
(cinnamic acid), 
$C_6Cl_4\left\langle\begin{matrix}COOH\\COOH\end{matrix}\right.$
(phenylacrylic acid).

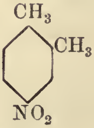
The nitro-compounds are those in which the hydrogen in the hydrocarbon is substituted by the nitro-radical, (NO_2), which, as may be conceived, imparts acid properties to the compounds. The leading members are—

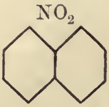
Nitrobenzene, $C_6H_5NO_2$ 

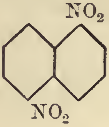
m.-dinitrobenzene, $C_6H_4(NO_2)_2$ 

o.- and p.-nitrotoluene, $C_6H_4CH_3NO_2$ 

Dinitrotoluene, $C_6H_4CH_3(NO_2)_2$ 1 : 2 : 4 

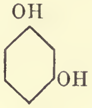
Nitroxylol, $C_6H_3(CH_3)_2NO_2$ 1 : 3 : 4 

α-nitronaphthalene, $C_{10}H_7NO_2$ 

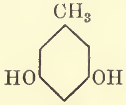
α-dinitronaphthalene, $C_{10}H_6NO_2$ 

The substitution products dealt with have been mainly the monosubstitution products, 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-radical occurs the chief are—

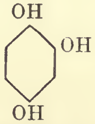
Resorcinol, $C_6H_4(OH)_2$



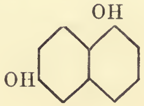
Oranol, $C_6H_3\begin{cases}CH_3\\OH\end{cases}$



Pyrogallol, $C_6H_3(OH)_3$



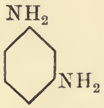
The dioxynaphthols, of which there are ten, $C_{10}H_6(OH)_2$



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

The phenylene diamines, $C_6H_4(NH_2)_2$

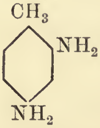
o,



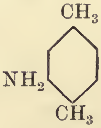
p,

The tolylene diamines, $C_6H_4CH_3(NH_2)_2$

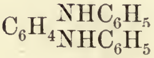
(1 : 2 : 4)

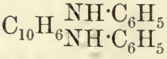


(1 : 2 : 5)

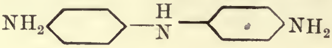


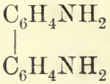
With this class the diamines in which substitution has already taken place in the amido-radical may be considered; *e.g.*—

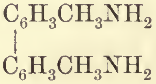
Diphenyl m.-phenylenediamine,

$C_6H_4\begin{matrix}NHC_6H_5\\NHC_6H_5\end{matrix}$

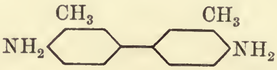
Diphenyl p.-naphthylenediamine,

$C_{10}H_6\begin{matrix}NH\cdot C_6H_5\\NH\cdot C_6H_5\end{matrix}$

Diamido-diphenylamine, $NH(C_6H_4NH_2)_2$

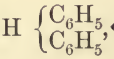


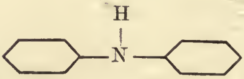
Benzedine,

$\begin{matrix}C_6H_4NH_2\\|\\C_6H_4NH_2\end{matrix}$

Toluidine,

$\begin{matrix}C_6H_3CH_3NH_2\\|\\C_6H_3CH_3NH_2\end{matrix}$

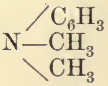


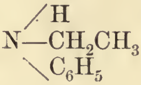
Among the secondary and tertiary amido-derivatives are found—

Diphenylamine,

$NH\begin{cases}C_6H_5\\C_6H_5\end{cases}$,

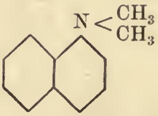


Benzlaniline, $C_6H_5NCH_2C_6H_5$,

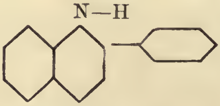
Dimethylaniline,

$N\begin{matrix}/C_6H_3\\—CH_3\\\backslash CH_3\end{matrix}$

Monoethylaniline,

$N\begin{matrix}/H\\—CH_2CH_3\\\backslash C_6H_5\end{matrix}$

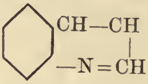
Dimethyl-α-naphthylamine, $C_{10}H_7N(CH_3)_2$,



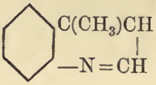
Phenyl-α-naphthylamine, $C_{10}H_7NHC_6H_5$



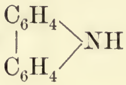
Quinoline, C_9H_7N



Quinaldine, $C_{10}H_9N$



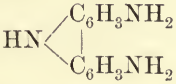
Carbazol, $C_{12}H_9N$



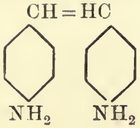
$\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix} > NH$

Orthomethyl benzene,
$C_6H_4NH_2(1:4)$
$C_6H_3(CH_3)NH_2$ (1 : 3 : 4)

Diamido carbazol,

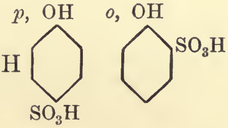


p.-diamido stelbine, $C_6H_4(NH_2)CH : CH \cdot C_6H_4NH_2$

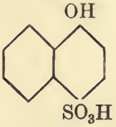


The sulphonic acids of the amido- and hydroxy-derivatives are of the utmost importance, often occurring in the molecule of colouring matters. The chief phenol-sulphonic acids are—

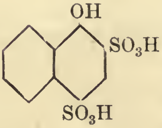
o. and p.-phenol sulphonic acid, $C_6H_4SO_3HOH$



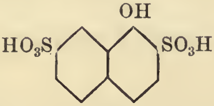
The α-naphthol monosulphonic acids, $C_{10}H_6{}^{SO_3H}_{OH}$, of which there are several isomers, but the most important is a naphthol monosulphonic acid, NW, ·1 : 4



The α-naphthol disulphonic acids, $C_{10}H_5{}^{(HSO_3)_2}_{OH}$, of which of the many isomers (1 : 2 : 4) are the principal

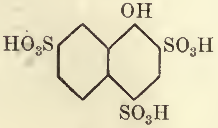


and (1 : 2 : 7)

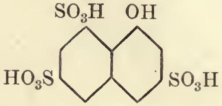


The *a*-naphthol trisulphonic acids, of which the following two are most commonly met with—

a-naphthol trisulphonic acid, 1 : 2 : 4 : 7

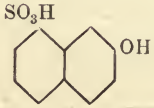


a-naphthol trisulphonic acid, 1 : 3 : 6 : 8



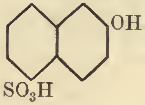
The *β*-naphthol monosulphonic acids, four of which are generally in use, namely—

Bayer's acid, $C_{10}H_6{}^{OH}_{SO_3H}(2:8)$

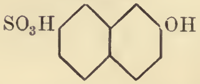


Schaffer's acid, $C_{10}H_6{}^{OH}_{SO_3H}(2:6)$

Dahl's acid, $C_{10}H_6{}^{OH}_{SO_3H}(2:5)$



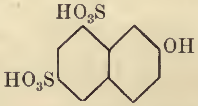
Cassella's acid, $C_{10}H_6{}^{OH}_{SO_3H}(2:7)$



The *β*-naphthol disulphonic acids. Of the many isomers, the following are of most importance—

β-naphthol disulphonic acid, $C_{10}H_3OH(SO_3H)_2$ 2 : 3 : 6

β-naphthol disulphonic acid, $C_{10}H_5OH(SO_3H)_2$ (2 : 6 : 8)



β-naphthol trisulphonic acid, $C_{10}H_4OH(SO_3H)_3$, most probably

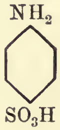
2 : 3 : 6 : 8

The sulphonic acids of the dioxynaphthalenes are important derivatives of this group, and give rise to many isomers, and those in use are believed to be various mixtures whose exact constitution is not known.

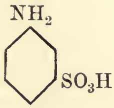
The amido-sulphonic acids are equally important with the hydroxy-sulphonic acids. The principal members that are of concern in lake manufacture are—

The sulphanilic acids, $C_6H_4NH_2SO_3H$

p,



m,



Phenylhydrazine p.-sulphonic acid, $C_6H_4NHNH_2SO_3H$

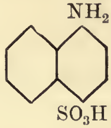
The toluidine sulphonic acids, $C_6H_3(CH_3)(NH_2)SO_3H$

The xylidine sulphonic acids, $C_6H_2(CH_3)_2(NH_2)SO_3H$

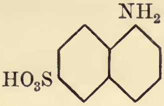
The α-naphthylamine sulphonic acids, $C_{10}H_6NH_2SO_3H$, of the seven isomers of which (1 : 4), (1 : 3), (1 : 6), (1 : 8), and (1 : 2) occur by far the oftener in colour molecules.

α-naphthylamine sulphonic acid

1 : 4



(1 : 6)

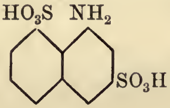


etc.

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

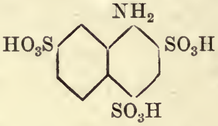
α-naphthylamine disulphonic acid, $C_{10}H_5NH_2(SO_3H)_2$

1 : 3 : 8



α-naphthylamine trisulphonic acid, $C_{10}H_4NH_2(SO_3H)_3$

(1 : 2 : 4 : 7)

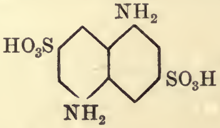


The β-naphthylamine mono- di- and trisulphonic acids are equally important to those of α-naphthylamine, and their constitution is similar, save that the amido group is in the β-position.

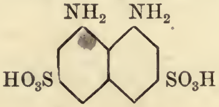
Referring to the sulphonic acids of the diamines, and the secondary and tertiary amines, the following are found of importance:—

Methyl and ethyl β-naphthylamine sulphonic acid,
$C_{10}H_6SO_3HNHCH_3$ and $C_{10}H_6SO_3HNHCH_2CH_3$
Diamido-naphthalene disulphonic acids, $C_{10}H_4(NH_2)_2(SO_3H)_2$

1 : 5 : 3 : 7

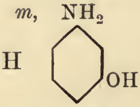


and (1 : 8 : 3 : 6)



The amido-phenols, that is, those compounds in which both the hydroxy- and the amido-radicals occur—

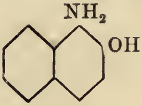
The amido-phenols, $C_6H_4NH_2OH$



and derivatives such as dimethyl-amido-phenol, $C_6H_4\left\langle\begin{array}{l}N(CH_3)_2\\OH\end{array}\right.$, and diethyl-amido-phenol, $C_6H_4\left\langle\begin{array}{l}N(C_2H_5)_2\\OH\end{array}\right.$, from which are derived the nitroso-compound, *e.g.*, $C_6H_3\begin{array}{l}/NO\\—OH\\\backslash N(CH_3)_2\end{array}$

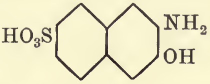
The amido-naphthols, of which there are several, which are largely used in the preparation of azo colours, the general formula of which may be expressed in this manner—

$C_{10}H_6OHNH_2(1 : 2)$

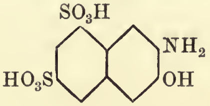


These amido-naphthols, as can be readily surmised, give rise to a series of mono- di- and trisulphonic acids, which are of great importance in the production of the above-mentioned azo colours. There are many isomers; they may be written thus—

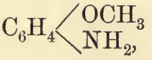
The monosulphonic acids, $C_{10}H_5NH_2OHSO_3H(2:3:7)$

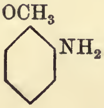


The disulphonic acids, $C_{10}H_4NH_2OH(SO_3H)_2(2:3:6:8)$

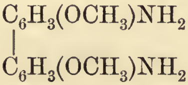


Among the derivatives of the amido-phenols may be counted anisidine, the methyl ether of amido-phenol,


$$C_6H_4{<}\begin{matrix}OCH_3\\NH_2,\end{matrix}$$



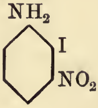
and dianisidine,


$$\begin{array}{l}C_6H_3(OCH_3)NH_2\\ |\\ C_6H_3(OCH_3)NH_2\end{array}$$

The amido-nitro-compounds are of considerable importance, among which occur—

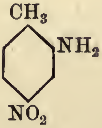
The nitranilines, $C_6H_7NH_2NO_2$,

m,



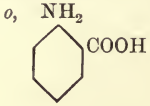
p,

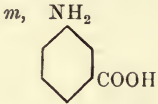
The nitrotoluidines, $C_6H_4NH_2NO_2$,



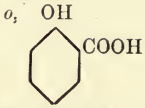
The multisubstitution products containing the carboxyl-radical, COOH, and its derivatives. The following are some of the best examples:—

Amido-benzoic acid, $C_6H_4NH_2COOH$





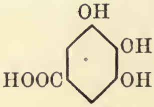
Salicylic acid, $C_6H_4(OH)COOH$



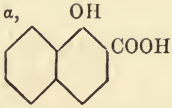
Amido-salicylic acid, $C_6H_3(OH)(NH_2)COOH$

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

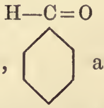
Gallic acid, trioxybenzoic acid, $C_6H_2(OH)_3COOH$

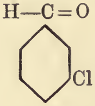


Naphthol carboxylic acid,

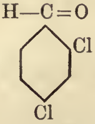


The introduction of the oxidation products of the fatty hydrocarbons, *i.e.*, the aldehydes, ketones, etc., give rise to a series of compounds, of which those of the greatest importance are—

Benzaldehyde, C_6H_5CHO,  and its derivatives, mono- and dichlorbenzaldehyde, C_6H_4ClCOH

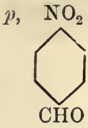


and $C_6H_3Cl_2CHO(1:2:4)$

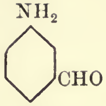


There are of course hydroxy- nitro- and amido-derivatives, of which the following are of considerable interest; *e.g.*—

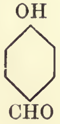
The nitro-benzaldehydes, $C_6H_4(NO_2)CHO$



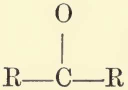
The amido-benzaldehydes, $C_6H_4(NH_2)CHO$ *m*,



The oxybenzaldehydes, $C_6H_4(OH)CHO$ *p*,



Of the ketones,



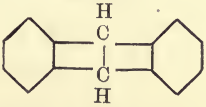
$R-\overset{\overset{O}{|}}{C}-R$

the following are of interest:—

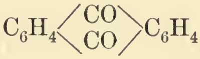
Benzophenone, $C_6H_5{\cdot}C{\cdot}O{\cdot}C_6H_5$, and its derivatives, the amido-benzophenones, $C_6H_5{\cdot}COC_6H_4NH_2$

diamido-benzophenones, $C_6H_4NH_2{\cdot}C:O{\cdot}CH_4NH_2$

The oxidation of anthracene, $C_{14}H_{10}$



gives rise to anthraquinone, from which the alizarine colours are derived. Anthraquinone, $C_{14}H_8(CO)_2$ or



$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_4$ or

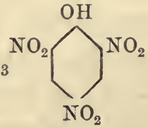
The preceding short sketch of the combinations of the various hydrocarbons has been given in order to illustrate how the combinations occur, and is to render the constitutional formula of the various colours more easily understood, and to enable the lake-maker to dissect the constitution of the colour, in order that he may apply, not merely the precipitating agent of the colour, but convert it into a true lake. To enter into theoretical considerations, and the various 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 production, and they can be better understood by the study of some standard systematic work on organic chemistry.

CHAPTER II

THE GROUPS OF THE ARTIFICIAL COLOURING MATTERS

The Nitro Group.—The chromophor of this group is the nitro-radical, NO_2, 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 use that the colours of this group are usually put to in lake-making is to modify the shade of basic colours with which they combine; in some cases totally precipitating, but usually only partially doing so—the precipitation of the basic colours by other means usually carries down the whole of the colours. Certain members combine partially with aluminium hydrate, $Al_2(OH)_6$, but on heating and washing are nearly entirely redissolved. Of the colours in this group those most generally met with are—

Picric acid, $C_6H_2OH(NO_2)_3$



Naphthol yellow dinitro-*α*-naphthol, $C_{10}H_5OH(NO_2)_2$, which usually comes into commerce as the sodium salt, $C_{10}H_5ONa(NO_2)_2$. Naphthol yellow S, the sulphonic acid of naphthol yellow, $C_{10}H_4(OH)(NO_2)_2SO_3H$, the sodium salt of which, $C_{10}H_4ONa(NO_2)_2SO_3Na$, is usually sold, combines with freshly precipitated aluminium hydrate, partially forming a pale yellow lake. A more complete precipitation takes place when the requisite quantity of barium chloride is used. When used with purely basic colours it is precipitated along with them, but after a time separates out; the most complete precipitation takes place when it is used in conjunction with amido-sulphonic-azo colours, 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 the aluminium hydrate, and on the addition of the barium chloride forms a compound lake. Green lakes produced in this manner are much faster to light than those produced by using other yellow dyestuffs.

The azo-dyestuffs are distinguished by the fact that they contain the chromophor, $—N = N—$, linked up to two benzene rings or other aromatic hydrocarbons, differing from the diazo compounds, which are similarly constituted, but not always combined with aromatic hydrocarbons. They form several well-defined groups, which may be classified as follows:—

(1) Amido-azo colour.
(2) Oxy-azo colours.
(3) Tetrazo dyestuffs.

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

Before proceeding to consider the various groups of the azo-colours, as these colours are by far the most numerous of the artificial dyestuffs, it will be as well to briefly discuss their general formation and the influence exercised on the colouring powers and properties by the various hydrocarbons and their substitution products when introduced into the colour molecule.

The azo-compounds, though mostly highly coloured bodies, are not really dyestuffs, unless they contain some body which imparts acid or basic properties to the compound. For instance, azo-benzene, though a brilliantly coloured body, does not possess dyeing properties, but when it is sulphonated, *i.e.*, converted into the sulphonic acid of azo-benzene, it acquires tinctorial powers, which, however, are considerably increased by the introduction of an auxochrome group like (OH). The introduction of the amido-radical confers basic properties on the compound; and whereas the acid azo-compounds have to be sulphonated to render them soluble, the basic are usually soluble. Combining with acids, however, to form salts, the introduction of the various auxochrome groups exercise great influence on the colour produced, more especially if they be of an entirely different nature to those already constituting the colour.

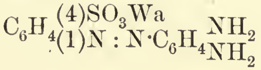
The compounds which contain only hydrocarbons of the benzene series are yellow, orange, and brown. When naphthalene is introduced they become red; and as the number of naphthalene rings increase they become bluer, yielding violets and various shades of blue.

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

To attempt to give a detailed list of the colours of this division alone would not be to any great advantage, as they are detailed in many lists and dictionaries,[1] and as a general rule they can be regarded as members of the same family, answering to the same reactions as regards precipitation and lake-forming. It is proposed to deal with the chief representatives only:—

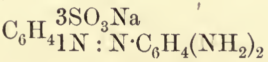
Chrysoidine diamido-azo-benzene, $C_6H_4\cdot N:N\cdot C_6H_3(NH_2)_2$

Diphenylamine orange or acid yellow D, sodium salt of p.-sulphobenzene-azo-diphenylamine,



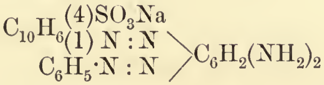
$$C_6H_4\begin{array}{l}(4)SO_3Wa\\(1)N:N\cdot C_6H_4\begin{array}{l}NH_2\\NH_2\end{array}\end{array}$$

Metanil yellow, the meta-sodium salt of sulphobenzene-azo-diphenylamine,



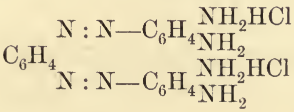
$$C_6H_4\begin{array}{l}3SO_3Na\\1N:N\cdot C_6H_4(NH_2)_2\end{array}$$

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



$$\left.\begin{array}{r}C_{10}H_6\begin{array}{l}(4)SO_3Na\\(1)\,N:N\end{array}\\C_6H_5\cdot N:N\end{array}\right\rangle C_6H_2(NH_2)_2$$

Bismarck brown, hydrochloride of benzene disazo-phenylene-diamine,



$$C_6H_4\begin{array}{l}N:N-C_6H_4\begin{array}{l}NH_2HCl\\NH_2\end{array}\\N:N-C_6H_4\begin{array}{l}NH_2HCl\\NH_2\end{array}\end{array}$$

When the 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.

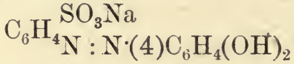
When the sulphonic acid group is present, barium chloride

---

[1] Two very good works of reference to the constitution, formula, and properties of the artificial colours are Schultze and Julius' *The Systematic Survey of the Organic Colouring Matters* and Hurst's *Dictionary of the Coal Tar Colours*, the former being the more scientific.

precipitates the bulk of the colour in most cases, but the precipitation is usually not complete; but the previous 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 resorcin yellow, the sodium salt of p.-benzene-azo-resorcinol,



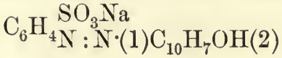
$$C_6H_4\begin{matrix}SO_3Na\\N:N\cdot(4)C_6H_4(OH)_2\end{matrix}$$

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 β-naphthol are found to be more permanent than those of a-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, which with the higher homologues become red; with the derivatives of naphthalene reds, which become bluer as the molecular weights of the compounds become greater. The colours known as the coccinines are derived from diazoanisol and its homologues and β-naphthol di-sulphonic acid.

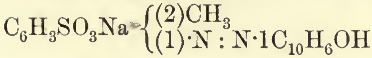
The colours belonging to this group are very numerous, varying from yellows to deep bluish-reds. Of those which demonstrate the constitution of this group the following examples are given:—

Orange 2.—Sodium salt of p.-sulphobenzene-azo-β-naphthol,



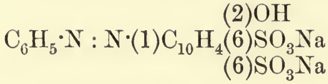
$$C_6H_4\begin{array}{l}SO_3Na\\N:N\cdot(1)C_{10}H_7OH(2)\end{array}$$

Mandarin G. R.—Sodium salt of sulpho-p.-toluene-azo-β-naphthol,



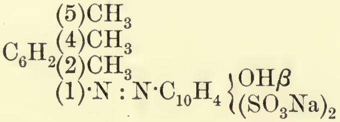
$$C_6H_3SO_3Na\begin{cases}(2)CH_3\\(1)\cdot N:N\cdot 1C_{10}H_6OH\end{cases}$$

Ponceau 2 G.—Sodium salt of benzene-azo-β-naphthol disulphonic acid,



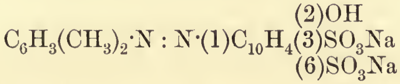
$$C_6H_5\cdot N:N\cdot(1)C_{10}H_4\begin{array}{l}(2)OH\\(6)SO_3Na\\(6)SO_3Na\end{array}$$

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



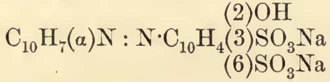
$$C_6H_2\begin{array}{l}(5)CH_3\\(4)CH_3\\(2)CH_3\\(1)\cdot N:N\cdot C_{10}H_4\begin{cases}OH\beta\\(SO_3Na)_2\end{cases}\end{array}$$

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



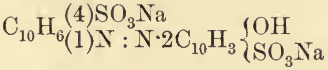
$$C_6H_3(CH_3)_2\cdot N:N\cdot(1)C_{10}H_4\begin{array}{l}(2)OH\\(3)SO_3Na\\(6)SO_3Na\end{array}$$

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



$$C_{10}H_7(\alpha)N:N\cdot C_{10}H_4\begin{array}{l}(2)OH\\(3)SO_3Na\\(6)SO_3Na\end{array}$$

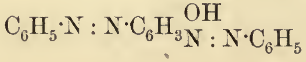
Crocein scarlet B. X.—Sodium salt of sulphonaphthalene-azo-β-naphthol monosulphonic acid,



$$C_{10}H_6\begin{array}{l}(4)SO_3Na\\(1)N:N\cdot 2C_{10}H_3\begin{cases}OH\\SO_3Na\end{cases}\end{array}$$

The tetrazo or disazo colouring matters are of a much more complex formation, and differ from the azo colours by containing the chromogen $\cdot N:N\cdot$ more than once in the molecule, and 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,

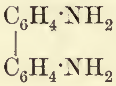


$$C_6H_5\cdot N:N\cdot C_6H_3\begin{array}{l}OH\\N:N\cdot C_6H_5\end{array}$$

(*b*) Those which contain the disazo groups in one ring and the auxochromes in the others. Tetrazo-benzene-phenol,

$$C_6H_5\cdot N:N\cdot C_6H_4\cdot N:N\cdot C_6H_4OH$$

(*c*) The disazo dyestuffs derived from benzidine,

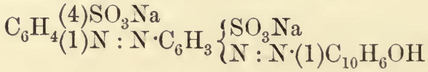


$$\begin{array}{l}C_6H_4\cdot NH_2\\ \vert\\ C_6H_4\cdot NH_2\end{array}$$

and its homologues.

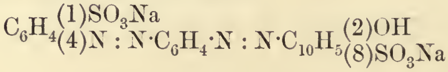
Without entering into minute detail concerning the formation and the chemical peculiarities of each of these groups, their general formation may be represented by the following few examples of this extremely numerous group:—

Biebrich scarlet. — Sodium salt of sulphobenzene-azo-sulphobenzene-azo-β-naphthol,



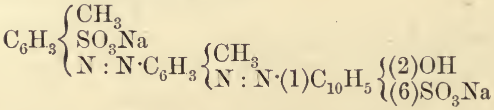
$$C_6H_4\begin{array}{l}(4)SO_3Na\\(1)N:N\cdot C_6H_3\begin{cases}SO_3Na\\N:N\cdot(1)C_{10}H_6OH\end{cases}\end{array}$$

Ponceau 4 R. B.—Sodium salt of sulphobenzene-azo-benzene-β-naphthol monosulphonic acid,



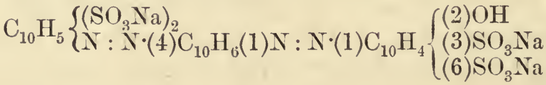
$$C_6H_4\begin{array}{l}(1)SO_3Na\\(4)N:N\cdot C_6H_4\cdot N:N\cdot C_{10}H_5\begin{array}{l}(2)OH\\(8)SO_3Na\end{array}\end{array}$$

Bordeaux G.—Sodium salt of sulphotoluene-azo-toluene-azo-β-naphthol-β-sulphonic acid,



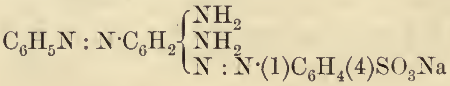
$$C_6H_3\begin{cases}CH_3\\SO_3Na\\N:N\cdot C_6H_3\begin{cases}CH_3\\N:N\cdot(1)C_{10}H_5\begin{cases}(2)OH\\(6)SO_3Na\end{cases}\end{cases}\end{cases}$$

Naphthol black 6 G.—Sodium salt of disulphonaphthalene-azo-α-naphthalene-azo-β-naphthol disulphonic acid,



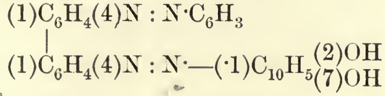
$$C_{10}H_5\begin{cases}(SO_3Na)_2\\N:N\cdot(4)C_{10}H_6(1)N:N\cdot(1)C_{10}H_4\begin{cases}(2)OH\\(3)SO_3Na\\(6)SO_3Na\end{cases}\end{cases}$$

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



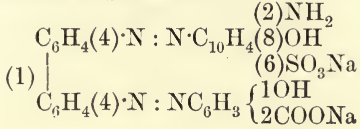
$$C_6H_5N:N\cdot C_6H_2\begin{cases}NH_2\\NH_2\\N:N\cdot(1)C_6H_4(4)SO_3Na\end{cases}$$

Cloth brown G.—Sodium salt of diphenyl-disazo-dioxynaphthalene salicylic acid,



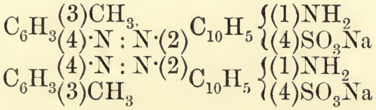
$$\begin{array}{l}(1)C_6H_4(4)N:N\cdot C_6H_3\\ \quad|\\ (1)C_6H_4(4)N:N\cdot\!-\!(\cdot1)C_{10}H_5\begin{matrix}(2)OH\\(7)OH\end{matrix}\end{array}$$

Diamine fast red.—Sodium salt of diphenyl-disazo-salicylic-amido-naphthol sulphonic acid,



$$\begin{array}{l}C_6H_4(4)\cdot N:N\cdot C_{10}H_4\begin{matrix}(2)NH_2\\(8)OH\\(6)SO_3Na\end{matrix}\\ (1)\;|\\ C_6H_4(4)\cdot N:NC_6H_3\begin{cases}1OH\\2COONa\end{cases}\end{array}$$

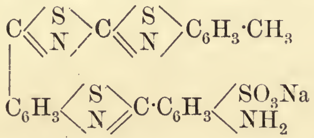
Benzopurpurin 4 B.—Sodium salt of ditolyl-disazo-binaphthionic acid,



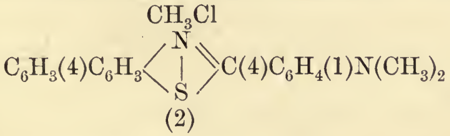
$$\begin{array}{l}C_6H_3\begin{matrix}(3)CH_3\\(4)\cdot N:N\cdot(2)\end{matrix}C_{10}H_5\begin{cases}(1)NH_2\\(4)SO_3Na\end{cases}\\ C_6H_3\begin{matrix}(4)\cdot N:N\cdot(2)\\(3)CH_3\end{matrix}C_{10}H_5\begin{cases}(1)NH_2\\(4)SO_3Na\end{cases}\end{array}$$

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

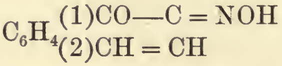
Primuline is a mixture of which the chief constituent is



Thioflavin-dimethyl-dihydrothiotoluidene-methyl chloride,



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, beyond the sulphonic-acid groups, leads to the necessity of adopting further reagents to procure, in some cases, the complete precipitation of the colour, and to increase its fastness and brilliancy, the consideration of which, together with the formation of a series of pigments of growing importance, *i.e.* the production of insoluble azo-colours on suitable bases, will be more fully considered later. The nitroso and iso-nitroso colours are an unimportant group, from which lakes are rarely made. They contain the chromogen ·NOH. About the best-known member is gambine β-nitroso α-naphthol

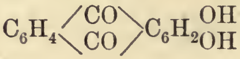


$$C_6H_4\begin{matrix}(1)CO{-}C = NOH \\ (2)CH = CH\end{matrix}$$

The oxyketone group, however, 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, form powerful colouring matters,—these colours have, however, to be united to metallic oxides before their full colouring power and shade are developed.

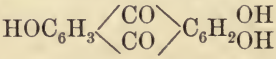
The derivatives of benzene and naphthalene are known, but they are of much less importance than those of anthracene, the principal colouring matters derived from this hydrocarbon being—

Alizarine V1.—α-β-dihydroxy-anthraquinone,



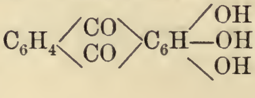
$$C_6H_4\left\langle\begin{matrix}CO \\ CO\end{matrix}\right\rangle C_6H_2\begin{matrix}OH \\ OH\end{matrix}$$

Alizarine RG.—Trihydroxy-anthraquinone,



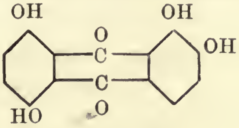
$$HOC_6H_3\left\langle\begin{matrix}CO \\ CO\end{matrix}\right\rangle C_6H_2\begin{matrix}OH \\ OH\end{matrix}$$

Purpurin.—Trihydroxy-anthraquinone,

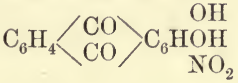


$$C_6H_4\left\langle\begin{matrix}CO \\ CO\end{matrix}\right\rangle C_6H\begin{matrix}/OH \\ -OH \\ \backslash OH\end{matrix}$$

Alizarine Bordeaux.—β-tetrahydroxy-anthraquinone,

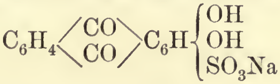


Alizarine orange.—β-nitro-alizarine,



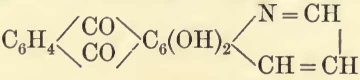
$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H\begin{matrix}OH\\OH\\NO_2\end{matrix}$$

Alizarine WS.—Sodium salt of alizarine monosulphonic acid,



$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H\begin{cases}OH\\OH\\SO_3Na\end{cases}$$

Alizarine blue.—Dihydroxy-anthraquinone-quinoline,



$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6(OH)_2\left\langle\begin{matrix}N=CH\\ \quad\ \ |\\ CH=CH\end{matrix}\right.$$

Alizarine indigo blue. — The sodium bisulphite compound of penta-hydroxy-anthraquinone-quinoline.

Great care has to be taken 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:—

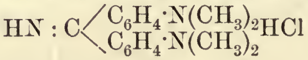
Dissolving the alizarine in a mixture of carbonate and phosphate of soda, adding the requisite quantity of oil, and carefully precipitating in the cold with sulphate of aluminium, adding a calculated amount of acetate of calcium, and developing the shade by slowly raising to the boil in the course of about three hours, and boiling one hour.

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

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

The ketonomides 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.

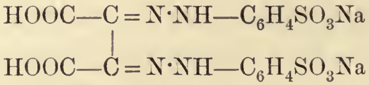
The chromophor is HN : C, the generally accepted formula of auramine being



$$HN : C\langle\begin{matrix}C_6H_4\cdot N(CH_3)_2HCl\\ C_6H_4\cdot N(CH_3)_2\end{matrix}$$

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 great use in lake-making for modifying the tones of the more powerful triphenylamine colours.

The hydrazene colour, tartrazine, is the sodium salt of sulpho-phenyl-hydrazide of dioxytartaric acid,



$$\begin{array}{l}HOOC—C=N\cdot NH—C_6H_4SO_3Na\\ \qquad\quad\;|\\ HOOC—C=N\cdot NH—C_6H_4SO_3Na\end{array}$$

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

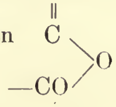
Triphenylamine Colours.—In this group occur nearly all the basic artificial colours. They are usually very soluble, and of great colouring power, and, owing to the brilliant shades they produce, are largely used in the production of lakes. They are, however, as a general rule, extremely fugitive to light, 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 $\equiv C$ $—NH—$

(*b*) The rosolic acid dyestuffs, containing the chromogen $\equiv C—O—$

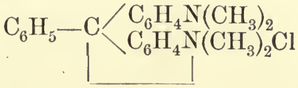
(*c*) The phthaleins, containing the chromogen



$$\begin{array}{l} \;\;\Vert \\ \;\;C \\ \quad\;\; \rangle O \\ —CO \end{array}$$

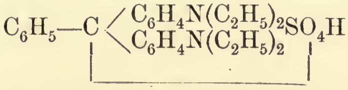
The following will be found to be representative members of the rosaniline dyestuffs :—

Malachite green.—Zinc double chloride of tetramethyl-p.-amidotriphenylcarbinol,



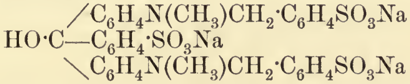
$$C_6H_5—C\begin{array}{l}\diagup C_6H_4N(CH_3)_2\\ \diagdown C_6H_4N(CH_3)_2Cl\end{array}$$

Brilliant green.—Sulphate of tetraethyl-diamido-triphenylcarbinol,



$$C_6H_5—C\begin{array}{l}\diagup C_6H_4N(C_2H_5)_2SO_4H\\ \diagdown C_6H_4N(C_2H_5)_2\end{array}$$

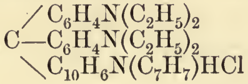
Acid green.—Sodium salt dimethyl-dibenzo-diamido-triphenylcarbinol trisulphonic acid,



$$HO{\cdot}C\begin{array}{l}\diagup C_6H_4N(CH_3)CH_2{\cdot}C_6H_4SO_3Na\\ —C_6H_4{\cdot}SO_3Na\\ \diagdown C_6H_4N(CH_3)CH_2{\cdot}C_6H_4SO_3Na\end{array}$$

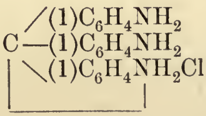
Guinea green B. — Sodium salt of diethyl-dibenyl-diamidotriphenylcarbinol disulphonic acid.

Night blue. — Hydrochloride of p.-tolyltetraethyl-triamidodiphenyl-*a*-naphthylcarbinol,



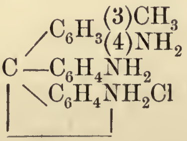
$$C\begin{array}{l}\diagup C_6H_4N(C_2H_5)_2\\ —C_6H_4N(C_2H_5)_2\\ \diagdown C_{10}H_6N(C_7H_7)HCl\end{array}$$

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



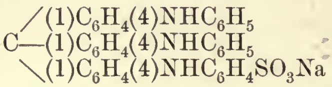
$$C\begin{array}{l}\diagup (1)C_6H_4NH_2\\ —(1)C_6H_4NH_2\\ \diagdown (1)C_6H_4NH_2Cl\end{array}$$

and



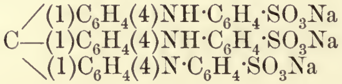
$$C\begin{array}{l}\diagup C_6H_3\begin{array}{l}(3)CH_3\\(4)NH_2\end{array}\\ —C_6H_4NH_2\\ \diagdown C_6H_4NH_2Cl\end{array}$$

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



$$\begin{array}{l} \diagup(1)C_6H_4(4)NHC_6H_5 \\ C{-}(1)C_6H_4(4)NHC_6H_5 \\ \diagdown(1)C_6H_4(4)NHC_6H_4SO_3Na \end{array}$$

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



$$\begin{array}{l} \diagup(1)C_6H_4(4)NH{\cdot}C_6H_4{\cdot}SO_3Na \\ C{-}(1)C_6H_4(4)NH{\cdot}C_6H_4{\cdot}SO_3Na \\ \diagdown(1)C_6H_4(4)N{\cdot}C_6H_4{\cdot}SO_3Na \end{array}$$

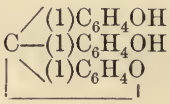
The basic dyestuffs of this group lend themselves to precipitation by various acids, such as tannic, oleic, phosphoric arsenious acids, producing lakes of varying stability and brilliancy. The most permanent are those produced from tannic acid, but they are far from being so brilliant, especially in the case of the magenta and green colours, as those produced by arsenious and oleic acid. 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 sulphonic 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.

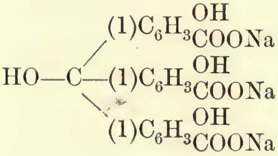
The colours from rosolic acid are not of very much importance, the chief representatives being—

Aurine or rosolic acid,



$$\begin{array}{l} \diagup(1)C_6H_4OH \\ C{-}(1)C_6H_4OH \\ |\diagdown(1)C_6H_4O \\ \underline{\qquad\qquad\qquad}| \end{array}$$

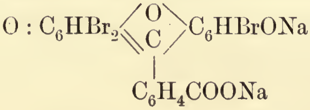
and chrome violet—sodium salt of aurine tricarboxylic acid,



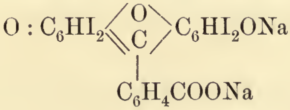
neither of which find any employment in the production of lakes.

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 of all the artificial colours. The general formula of the principal members may be represented by the following examples:—

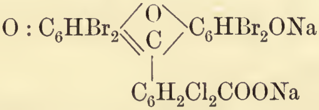
Eosine A.—Alkali salts of tetrabrom-fluoresceine,



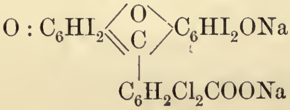
Erythrosine.—Alkali salts of tetraiodo-fluoresceine,



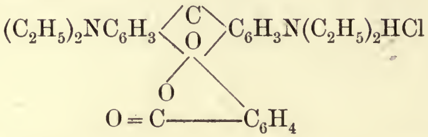
Phloxin.—Alkaline salts of tetrabromdichlor-fluoresceine,



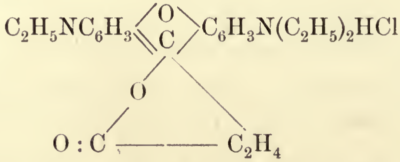
Rose Bengal.—Alkaline salts of tetraiododichlor-fluoresceine,



Rhodamine B.—Hydrochloride of diethyl in amido-phenolphthalein,

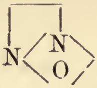


Rhodamine S.—Hydrochloride of diethyl in amido-phenolsuccineine,

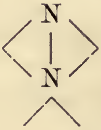


Other higher products of this group, such as gallein and coeruleine, are of more interest to the dyer, producing violet and green shades on mordanted goods, but are rarely used in lake-making.

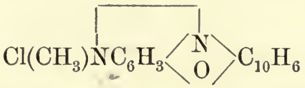
The oxazine, thioazine, and azine group of colours are the derivatives of rather a complex chromophor, which in the case of the oxazines may be shown as follows:—



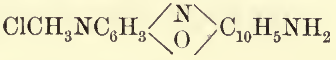
The thio or sulphur azines, as

The azines, as  which in the safranines become modified thus,  It contains a number of extremely valuable colouring-matters, mostly of a basic character, which give very useful lakes, the principal of which are—

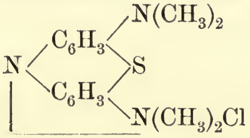
Fast blue 2 B.—Chloride of dimethyl-phenyl-ammonium-β-naphthoxazine,



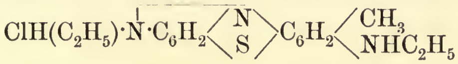
Nile blue A.—Chloride of dimethyl-phenyl-ammonium-α-amido-β-naphthoxazine,



Methylene-blue B.—Chlorides of tetramethyl thionine,



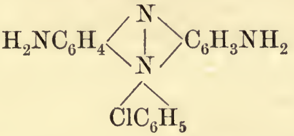
New methylene-blue.—Chloride of diethyl-toluthionine,



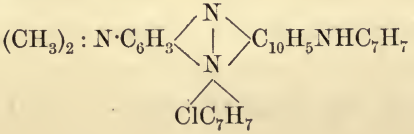
Of the azines the safranines are of the greatest interest. The indulines, though yielding lakes, are not much used by the lake-makers, as the shades produced are not very brilliant, and can more readily be obtained from other colours.

The general formation of the safranine group can be judged from the following examples. They are basic in nature, and give very good results with tartar emetic and tannic acid.

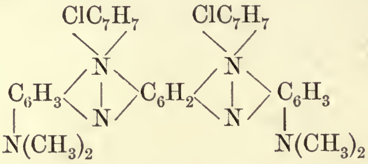
Safranine B.—Diamido-phenyl-phenazonium chloride,

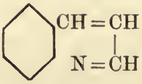
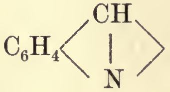


Basle blue R.—Dimethyl-amido-tolylamido-tolylphenon-naphthazarine chloride,

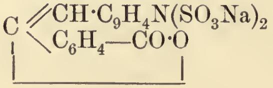


Metaphenylene-blue.—Tetramethyl-diamido-o-tolyl-diphenyl-azonium chloride,



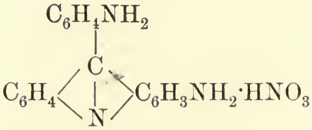
The tannic acid lakes of these colours are the best. The blues yield fine shades; the red shades are brighter and faster lakes than those produced from magenta, and are of great use in the production of bright maroon lakes, as they have not the same tendency to darken that magenta has. The quinoline and acridine colours are principally of interest because they yield us the quinoline yellow and the phosphines. Quinoline, C_9H_7N  and acridine,  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,



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,



$$\begin{array}{c} C_6H_4NH_2 \\ | \\ C_6H_4\left\langle \begin{array}{c} C \\ | \\ N \end{array} \right\rangle C_6H_3NH_2\cdot HNO_3 \end{array}$$

their general constitution can easily be understood.

Of the groups of artificial colours those described will be found to contain the colours mostly 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, and are not, or only very occasionally, dealt with when producing pigments; and for this reason many groups have been omitted entirely, not because they are unimportant, but that they have little or no interest compared with the other groups of artificial colours used for the purposes of precipitation.

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 in the main be regarded as almost pure derivatives of the colours.

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. This is done for several reasons, but mainly in order to reduce the strength of the colour, so as to enable larger quantities of the dyestuff to be used, and thus to diminish the danger of a slight error in weight causing a considerable alteration in the shade, and in order to approximate the price to competing colours. 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 dyehouse; but when used for the production of lake pigments, by entering into one or more of the reactions taking place in the formation of the lake, lead to results that are not expected, and 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; for the lake-maker requires only the tinctorial power from the colours, because by means of the bases used he dilutes the shade produced to the depth and strength required, and the presence of dilutants in the dyestuff, if they enter into any reaction during the lake-forming process, not only are misleading but actually increase the cost of production. The purer brands are often distinguished by the term extra; *e.g.*, rhodamine 6G extra is sold as being five times stronger than rhodamine 6G, but is considerably under five times the price of rhodamine 6G, for in Plate No. 1 (facing page 43), sample (1 : 2), it will be seen that a 10 per cent. lake of rhodamine 6G is considerably lighter than a 2 per cent. lake of rhodamine 6G extra.

The paste colours, as a rule, are those insoluble in water, such as the various alizarines, and usually contain 20 per cent. of the colouring-matter. These colours in many, but not all instances, can be obtained almost pure in powder, and it is advisable, for the reasons already stated, to use where it is possible the purer forms in preference to the pastes.

In selecting colours, it is advisable to buy only those colours which are the products of the leading colour-making firms, such as Read, Holliday & Sons, Badische Anilin und Sodafabrik; Brooke, Simpson & Spiller, L. Cassella, Actungesellschaft fur Anilinfabrikation, Berlin; Société pour l'Industrie Chimique, Basle; Kalle & Co., A. Leonhardt & Co., Geigy, Basle, and some others, as the majority of the colours made by these firms are well known, and can be found in the various lists and dictionaries of the coal-tar products, and from their recognised agents the colours required can be obtained, and little doubt need be exercised as regards their constitution and composition.

Experience has shown that for lake-making the eosines of the Badische A. S. F. are preferable to other makers.

The oranges and cheap shades of scarlet, together with the basic greens and magentas of the Berlin Company, are to be recommended.

The better class azo scarlets and oranges and acid greens of Meister Lucius & Brunning, and Read, Holliday & Sons, give lakes of a most satisfactory nature.

Comparison has shown there is but little to choose between the various brands of naphthols and amido bases, such as paranitraniline of the various makers; any preference that there is might be given to the naphthols and developers of Meister Lucius & Brunning, and the paranitraniline of L. Cassella & Co. The latter firm produce a number of scarlets admirably adapted for lake-making, but they have a tendency to give a less fiery red than others that are either cheaper or equivalently better; they, however, are well adapted, on account of their clean precipitation, for use in the production of deep shades, such as carnations and maroons.

The blues, basic and acid browns, and rhodamines of the Société pour l'Industrie Chimique have been found to yield the most satisfactory results.

The above recommendations have no reference to the properties of the various dyes, as regards their application to textile fabrics, but only to their use in the manufacture of lake pigments, and, though not referring to the superiority of any one maker's colours, are given merely as indications of the results of many hundreds of comparisons and trials of the colours produced by the various firms.

When colours are offered which do not bear the name of a recognised firm, they must always be looked upon with a certain amount of suspicion, as they are often sophisticated colours prepared for a special purpose, and are not to be relied on.

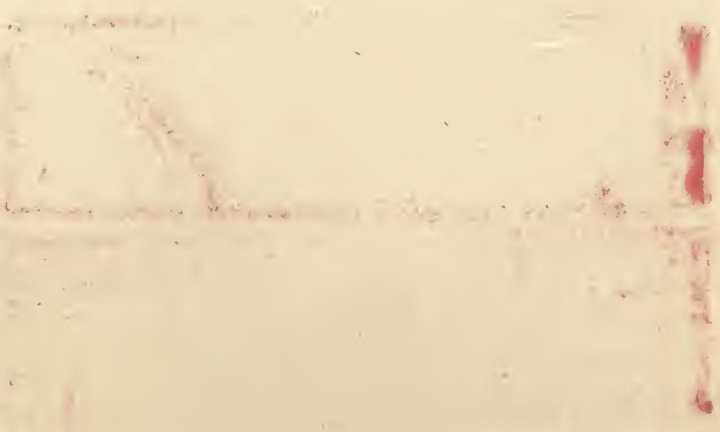
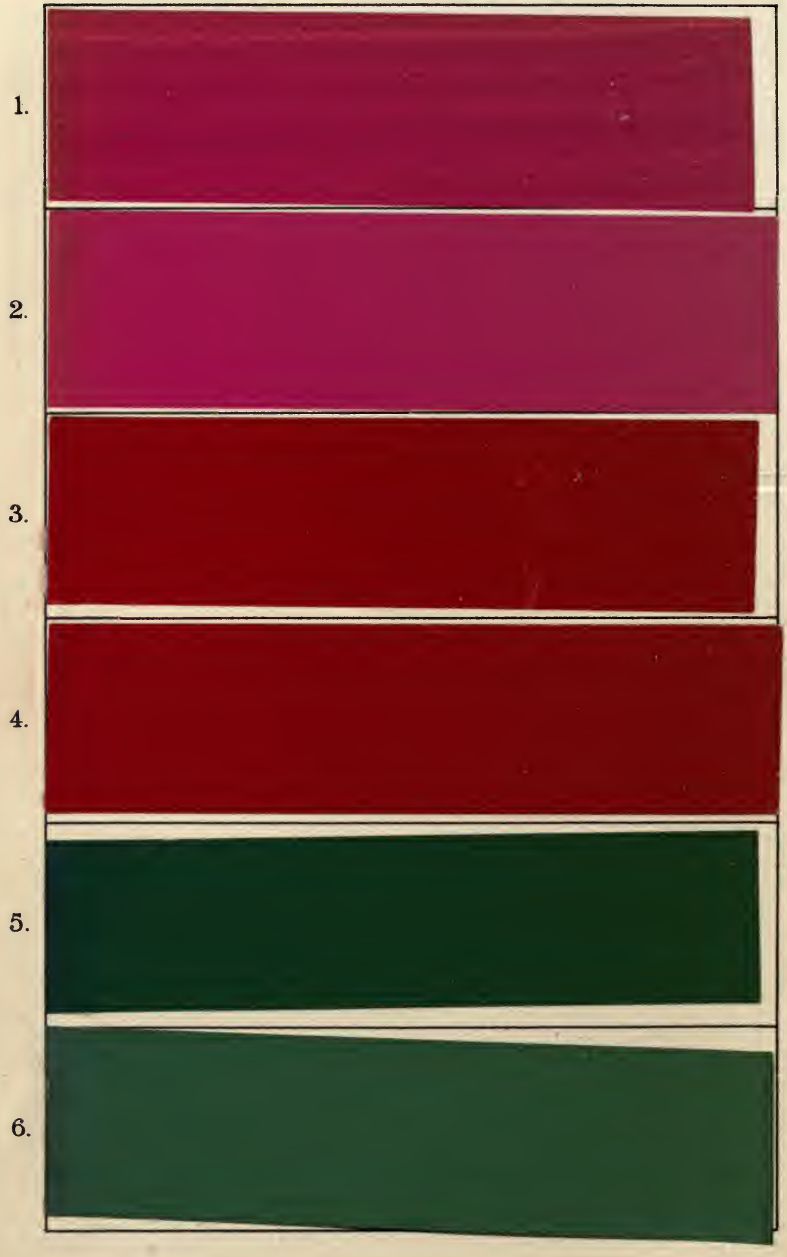


PLATE I.



Colours should always be dissolved in water by themselves, and then sieved into the precipitating tank through a fine sieve, about 80 meshes to the inch. The vessels used for the purpose of dissolving acid and basic colours of wood should be kept separate, as the strong basic colours often materially alter the shade of the finished lake if they come into contact, even in minute quantities, with acid colouring matters, or, worse still, produce dark tarry specks throughout the lake 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 separately, and added to the tank, a different shade is produced to that where all the colours are mixed together and added separately. This more especially applies to azo-acid colours, for as a rule basic colours are better dissolved separately, for if one contains an acid group, the other often acts upon it, producing a tarry precipitate that is very difficult to deal with.

On Plate No. 1 (opposite this page), samples 3 and 4 show in

3. A mixture of ponceau GL, ponceau 4RB, and orange II, dissolved together before precipitating;
4. The same colours dissolved separately and added together in the tanks before precipitation.

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, then add boiling water until the colour is entirely dissolved. Though boiling the colours does not usually injure them, it is better avoided, as in some cases, notably auramine, the colour is decomposed, and gives quite another shade to that expected, as will be seen from the samples Nos. 5 and 6 on Plate No. 1 (opposite this page).

5. Tannic and tartar lake of ethyl-green crystals and auramine O; the auramine boiled.
6. The same lake, the auramine dissolved in water at 90° C.

The best mode to dissolve the colours which are obtained in the crystalline form is 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 two gallons of water, and agitate until solution is complete.

The addition of soda or other materials to the water, in order to facilitate solution, is to be strongly deprecated, as it only induces difficulties which would otherwise be avoided.

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—nitrate and acetate.

Barium chloride is the typical lake-forming body for the sulphonic acids, forming the barium sulphonates of the colours which, in the greater number of cases, are insoluble in water. It is usually solid as the crystals, which are colourless rhombic prisms containing two waters of crystallisation, and therefore has the formula $BaCl_2 2H_2O$, molecular weight 243·46, and is soluble in about double its weight of water at the boil. It loses its water of crystallisation if heated to 113° C., fuses at a red heat, and, when fused in the presence of air, loses chlorine with the formation of baryta, and consequently the fused varieties have often an alkaline reaction.

It is made by dissolving witherite, mineral carbonate of barium, in hydrochloric acid, or, by fusing the barytes with carbon, limestone, and calcium chloride, lixiviating the mass with water to dissolve out the chloride, and crystallising.

A good sample should in mass appear almost pure white, and a single crystal should appear clear and transparent, and should on no account contain any iron salts, which will give a brownish hue to the bulk, and is easily detected by the addition of a little ferrocyanide solution to a solution of the chloride, when a bluish coloration will appear. 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 the manufacture. It should be carefully handled, as, taken internally, it is a very violent poison; and its solutions coming in contact with sores causes them often to slightly ulcerate, and be a considerable time in healing.

Caustic baryta, $Ba(OH)_2$, is used occasionally in the production of lakes, in order to procure the entire precipitation of colours which contain 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 in hot. It rapidly absorbs carbon dioxide, as a strong alkaline reaction, but is only used in special cases, and is not as a general thing found in the lake-maker's store.

Acetate of lead, $PbCh_3(COOH)_2 3H_2O$, molecular weight 378. It is extremely soluble, dissolving in eight times its own weight of cold water, and in its water of crystallisation at 75°·5 C. It crystallises in oblique rhombic prisms, and on exposure effloresces. From its sweet astringent taste it has obtained the name of sugar of lead. It 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 a fairly large size. There are some qualities very white to look at, and very fine crystals; this kind does not work very well, giving rise to excessive frothing, and, where the colours are used in size, it causes often very considerable annoyance by causing the lake, when being made up with this substance, to rise up and run 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 of the hydroxy compounds.

Nitrate of lead, $Pb(NO_3)_2 2H_2O$, molecular weight 366·1. It crystallises in regular octohedrons; it is fairly soluble in water, dissolving in about its own weight of water. Lead salts possess the power of precipitating a large number of dyestuffs, both sulphonic acids and triphenyl-methane colours; but, save for eosines and allied colours, their use is not to be advised, for, as well as being far more expensive than barium salts, the pigments given are as a rule much duller than those produced by other precipitating agents; but, in the cases where they are suitable, they demonstrate their suitability in no doubtful way. In many cases the precipitation is by far more complete with acetate of lead than with barium chloride, mainly due in all probability to the acetic acid being a much less potent acid than the hydrochloric of the barium salt. In any case, where precipitation was taking place simultaneously with the production 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 in such cases is prohibited. Yet, as will be seen, as 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 simply thrown down on inert bases.

The two salts of lead which are used for this purpose are the acetate and nitrate at 65° C. It is considerably cheaper than the acetate, and can in many cases be substituted for the acetate; 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 antimonious tartrate, better known as tartar emetic, $2C_4H_4O_6(SbO)K + H_2O$. It forms rhombic prisms soluble at the ordinary temperature in about fifteen parts, and at the boil in about three parts of water to one of colour. When heated to 200° to 220° C., it loses water, and forms $C_4H_2O_6SbK$, 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—

$$C_2H_2(OH)_2\left\langle\begin{matrix}CO\cdot O\\ CO\cdot O\end{matrix}\right\rangle SbOH$$

of which tartar emetic is the potassium salt.

This substance is largely used, both in dyeing and lake-making, for fixing lakes produced from basic colours by means of tannic acid. In the production 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 in 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 other fixing agent should be employed but tartar emetic, for of all tannic acid lakes they are the brightest and fastest.

The oxide of antimony, H_2O_3, is used in the same way as white arsenic, to precipitate basic colours by dissolving it in sodium carbonate, and precipitating the lake and the base together by adding the solution to a solution of aluminium sulphate and the colour, but it is but very little used for this purpose.

Zinc sulphate, $ZnSO_4 7H_2O$, white vitriol, is used to precipitate in some cases eosines, but not often. It is a white crystalline solid, fairly soluble in water; it is decomposed by the action of normal sodium carbonate into basic carbonates, and zinc hydrate. In some instances, notably the marine blue of ML and B and the erioglaucines, a small percentage of the mixed carbonate and hydrate so produced, mixed with the base, leads to much more of the colouring-matters being precipitated than otherwise would be the case.

Aluminium salts.—The salts of this metal, notably the sulphate and the acetate, are by far the most important reagents that the lake-manufacturer has at command; not so much that they readily precipitate the colouring-matters, because with very few exceptions the addition of an aluminium salt to the solution of a colouring-matter produces no apparent change, but because they form the source of aluminium hydrate, $Al_2(OH)_6$, which has the power to act as either an acid or a basic substance, and in consequence of this property is able to play the part of a powerful auxiliary in the precipitation of colouring matters, as well as to combine with other bodies to form insoluble aluminium compounds, which are an important class of lake bases.

Aluminium sulphate, $Al_2(SO_4)_{18}H_2O$. — This salt is extremely soluble in water; it, however, comes into the market in various forms, and very rarely in crystalline form, and is usually sold as guaranteed to contain a certain percentage of Al_2O_3. Lump aluminium sulphate usually contains from 11 to 16 per cent. of Al_2O_3; but these qualities are apt to contain a considerable quantity of iron. The best make is a fine dry white powder, containing about 17 per cent. of Al_2O_3, and this, and this alone, should be used in the manufacture of pigments, as it is much purer and more to be relied on than other qualities which are only a little cheaper in price.

The best guides in selecting a sulphate of aluminium are—the colour, which should be quite white; the percentage of Al_2O_3 it contains; and its freedom from iron. The presence of 0·5 per cent. Fe_2O_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—

$$Al_2(SO_4)_3 + Na_2CO_3 + H_2O = Al_2(SO_4)_2(OH)_2 + Na_2SO_4 + CO_2$$
$$Al_2(SO_4)_2(OH)_2 + Na_2CO_3 + H_2O = Al_2SO_4(OH)_4 + Na_2SO_4 + CO_2$$
$$Al_2SO_4(OH)_4 + Na_2CO_3 + H_2O = Al_2(OH)_6 + Na_2SO_4 + CO_2$$

If the solutions of sulphate and carbonate be very dilute and cold, until a considerable quantity of the sodium carbonate has been added no permanent precipitation takes place, as the basic sulphates formed do not separate at low temperatures. This property, as the basic sulphates have a very considerable attraction for basic colouring-matters, 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 the complete precipitation of the aluminium hydrate by adding slowly the requisite amount of soda and raising the temperature.

When the solutions are hot and concentrated, the precipitate is generally very lumpy, and if there be an excess of aluminium sulphate, a combination between the hydrate already formed and the excess takes place, giving the precipitate a semi-crystallised 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 aluminium sulphate. 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, as in the latter industry it is only substituted in those cases where the presence of the sulphuric acid is objectionable.

Hydrate of aluminium, $Al_2(OH)_6$.—This body is produced when caustic soda or potash, ammonium hydrate or carbonated alkalies are added to a solution of an aluminium salt; it is soluble in caustic alkalies, and therefore is usually obtained by means of the carbonates.

When produced from cold dilute solutions, it 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 it is much denser, 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 it takes up alone. Whether with hydroxy compounds the aluminium lake is more readily formed, or it 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 the mixture risen to the boil afterwards, fixes more colour than a sample produced hot from the same materials, and where 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 fairly concentrated; otherwise they dry very hard, instead of being friable.

Aluminium hydrate, when dried, forms a hard white horny substance, which has the composition of $Al_2(OH)_6$, and only on ignition is the whole of the water driven off, leaving Al_2O_3.

Of the tin salts, stannous chloride, $SnCl_22H_2O$, which crystallises in transparent monoclinic prisms. It dissolves in its water of crystallisation at 40° C. It is hydroscopic, and is only stable in concentrated solutions, decomposing on dilution, forming a basic chloride which is insoluble in water. It is but little used save with some few colours, as its powerful reducing action destroys the shade of many of the artificial colours, but forms the basis from which stannic acid compounds are prepared which are used in the preparation of special lakes from basic colours, especially greens and blues.

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

Sodium acetate, $CH_3COONa3H_2O$, is also largely used as an assistant in lake manufacture. It is introduced into the 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 to the stronger acids on the various ingredients of a lake pigment; and, secondly, its faint alkalinity in many cases enable the shade and brilliancy of the colour to be fully brought out, whereas if the solution were acid or alkaline with a free acid or alkali this objective would not be attained.

It crystallises in monoclinic prisms, and is soluble at the boil in about half its weight of water. A tartar emetic and tannic acid lake when made in the presence of this salt settle readily; if it be absent, there is sometimes considerable difficulty in washing the lake thoroughly, as the pigment either hangs or settles very slowly.

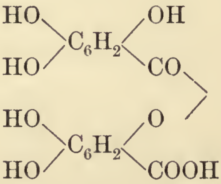
CHAPTER V

LAKE-FORMING BODIES' BASIC COLOURS

It will be found that the lakes formed from basic colours are combinations of the colour and some acid or semi-acid body. Just as the acid colours behave as if they were the acid of a simple salt, so the basic colours act as if they were the bases of the salts formed by their union with the acids. The acids most commonly used for this purpose are tannic, phosphoric, arsenious, antimonious, stannic, resinic, palmatic, stearic, and allied fatty acids.

The most important of these, as regards producing the fastest and most satisfactory lakes, is—

Tannic acid, digallic acid.—Tannin, $C_6H_2(OH)_3COOC_2H_6(OH)_2COOH$, is a weak astringent acid substance derived from gall nuts, which are formed by the action of insects on certain trees and shrubs, and in sumach, *i.e.* the twigs and leaves of an Italian shrub, from which it is prepared by extraction with water and alcohol. The constitution may be expressed by the following formula :—



It is sold in various brands, containing more or less tannic acid. A good variety only should be used for the formation of pigments, which should be of a pale yellowish-brown colour. It should be kept in closed vessels, as under the action of air and light it changes very considerably.

In alkaline solutions it absorbs oxygen, and darkens in colour; its aqueous solutions are precipitated by dilute mineral acids, save nitric sodium and potassium chloride and potassium acetate, but not by Glauber's salts.

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

Phosphoric acid, H_3PO_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, but a salt known commercially as phosphate of soda, which really is disodium hydrogen phosphate, $Na_2HPO_410H_2O$. This salt, when added to a solution of a basic dye, say methyl violet or a rhodamine, does not produce a precipitate, and the precipitation is only effected when an insoluble phosphate is thrown down, usually the aluminium salt.

Disodium hydrogen phosphate, though seemingly an acid salt, has a faintly alkaline reaction; but its salts are easily soluble in dilute acids, especially its aluminium calcium and barium salts, and when it is added to a solution of aluminium sulphate, a salt with an acid reaction, free acid is often liberated, which dissolves part of the precipitate, and renders that which remains slimy and unusable. If the solutions be rendered alkaline, precipitation takes place completely, but the colour is almost entirely redissolved. When using this salt it is advisable to add to it almost sufficient soda to neutralise any free acid that might be liberated, only enough to give a neutral, not an alkaline solution, but if anything very faintly acid. 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, and only 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, H_3AsO_3.—The solution of arsenic trioxide in water yields a solution of this acid, which, however, is very unstable; but its salts are extremely stable, and, as with phosphoric acid, its 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 produce any precipitation when added to a solution of a colouring-matter, say ethyl-green 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 only exercised when combined with some metal forming a complicated acid salt; and as such salts are formed when solutions of their alkaline salts are added to a solution of aluminium salts, it is to be assumed that these arsenical and phosphoric aluminium compounds fix the dye, and that it is not merely a case of precipitation by a poly-hydroxy acid, which is confirmed by the fact that an addition of colour to the thoroughly washed precipitate forms, by the interaction of a solution of aluminium sulphate, and an alkaline arsenite or phosphate is fixed by it.

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 the results are extremely various.

Stannic acid and meta-stannic acid are used to form lakes with basic colours. Meta-stannic acid, however, has but feeble attraction for colours, and is only used very occasionally. Stannic compounds are, however, used for the production of some green lakes. They are more brilliant than the tannic acid greens, but not equal to those produced by arsenious acid, but being more poisonous have in some instances preference given to them over arsenical lakes on that account.

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. These tin lakes require great care in their manipulation, and are rarely met with, though with the lakes from natural colours, such as fustic, Persian berries, etc., they are of considerable importance.

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

Resinic acid, or a solution of rosin in sodium carbonate, is largely used to produce brilliant magenta and green lakes by precipitating the basic colours together with a metallic resinate, such as the lead, zinc, or aluminium compound. The lakes are certainly very brilliant, and have a considerable demand among wall-paper manufacturers. The process adopted and the precautions to be observed are similar to those adopted in the making of phosphoric and arsenical lakes; but they are of no use for oil or lithographic work, and are about the most fugitive lakes produced from basic colours.

The use of various fatty acids, in the form of soaps, is not to be recommended as a sole method of precipitating basic colours; but considerable use is made of these acids, both in the form of soaps, or soluble preparations of the free acids, such as occur in the various sulphated and soluble oils, when amido-acid colours are being formed into lake pigments, as their property of combining with the basic groups fixes the colour better, 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.

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, and 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 that he can take advantage of; and for the same reason it is also simpler, because he has not to take into account the variations of the affinity for the colouring-matter of bases, as the wool-dyer has the various grades and classes of wool.

The bases used for this purpose are bodies insoluble in water, and are used either in the form mentioned, or are produced at the same time with the lake. The list given below embraces most of the substances used for this purpose:—

I. Barium sulphate, as barytes (natural) and blanc-fixe (precipitated), $BaSO_4$.
II. Clay.—China clay, a compound silicate of aluminium.

III. Calcium sulphate.—Paris white, gypsum (natural), satin white (precipitated), $CaSO_4$.
IV. Kieselguhr.
V. Red lead.
VI. Zinc oxide.
VII. Lead sulphate, $PbSO_4$.
VIII. Aluminium hydrate, $Al_2(OH)_6$.—Chalk, calcium carbonate, $CaCO_3$.
IX. Phosphate of aluminium, $AlPO_4$.—Aluminium arsenite.
X. Phosphate of barium, $Ba_3(PO_4)_2$.—Lead carbonate, white lead.
XI. Phosphate of calcium, $Ca_3(PO_4)_2$.
XII. Lamp and vegetable black (carbon).
XIII. Green earth.

They are introduced into the pigment either by suspending them in water and precipitating the lake on them, or by producing them and the lake at the same time, or by combination of the two methods, *i.e.*, 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 pure white, very finely ground, should be used. It possesses but little covering power in oil, and when used to make pigments for oil-work it is advisable to mix it with lead sulphate in the case of cheap goods, with lead carbonate and red lead (when shade allows) for better qualities. For some classes of pulp colours it is extremely valuable, as it gives very bright and full shades with, compared to other bases, small amounts of colouring-matter.

The precipitated variety is obtained by precipitating from a soluble barium salt the sulphate, by means of sulphuric acid. The fineness of the particles, on which the quality greatly depends, is varied according to the method of precipitation. Where the solutions have got too hot, or have been too concentrated, the product is liable to have a semi-crystalline appearance, and the particles are coarse in comparison to finer qualities. It is commercially known as blanc-fixe, permanent white, and enamel white. It is largely used as a base for pulp colours, as it gives a fine solid appearance, and, above all, works out on paper perfectly smoothly, differing from barytes, which, however finely ground, imparts a rough feeling to any pigment that it contains, which renders 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 produced on barytes being much fuller and brighter than that given by blanc-fixe, which is often of a different tone, besides being weaker and duller.

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, is a naturally occurring substance, being 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; it is capable of retaining about 60 per cent. of water, giving pulps of a smooth appearance and finish. Like barium sulphate, it has no attraction for colouring-matter, though it is often coloured by being saturated with solutions of colouring-matters, which, however, can be entirely removed by washing. In lakes where a large proportion of clay has been used, they are apt to have a chalky and bright appearance, which detracts very considerably from their appearance, and rather dulls the shade; also in the final washings it is apt to hang, taking a very considerable time to settle.

In combination with hydrate of aluminium these objectionable qualities mostly disappear. These combinations can be more readily discussed when dealing with other similar aluminium hydrate mixtures.

China clay is a much lighter substance than either gypsum and barytes, and is used mixed with these bodies, to make them lighter and diminish the coarseness of the gypsum and barytes. With some lakes, more especially the pulp lead eosine lakes, when mixed with blanc-fixe, it both makes the pulp less tenacious, 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. Naturally it occurs as $CaSO_4 + 2H_2O$; the whole of the water is driven off between 110°–120° F., and the residue is known as burnt gypsum or plaster of Paris, and can be readily identified by its property of combining with water; with evolution of heat and subsequently solidifying, when heated to above 200° C., it becomes dead burnt, and then only takes up water slowly, and does not harden.

It is slightly soluble in water, much more so in the presence of ammoniacal salts and sodium chloride, and fairly soluble in hydrochloric acid, which sometimes causes it to be overlooked in cursory examinations of lakes.

But for these properties it would be much preferred to barytes, which, though heavier and of much less covering power, is entirely insoluble; it is therefore but little used in the manufacture of lake pigments in the natural form; but satin white, precipitated calcium sulphate, is used pretty largely for the making of pulp satin colours, *i.e.*, those that readily on brushing take up a fine high glaze. Unfortunately, many red lakes, when on calcium bases, on being mixed with size bleed, and therefore in all cases it is not possible to use satin white. Satin white gives lakes of a heavier nature than clay, but considerably lighter than barium compounds.

Red lead, or minium, P_3O_4, litharge, PbO_2, and orange lead, Pb_2O_3, are mainly used in producing shades of vermilionettes and permanent reds in conjunction with other bases, such as barytes, lead sulphate, and carbonate, and other lakes which are used as paint, in order to modify the shade and improve the body and covering power.

Lead sulphate, $PbSO_4$, 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 and useful sulphate of lead, containing some impurities, and usually requiring well washing, can be obtained, known as lead bottoms, a bye-product obtainable from calico print-works and paper-works, which being a precipitated sulphate is very fine, and gives excellent results.

White lead, or lead carbonate, is but little used, and only for paint colours; its well-known properties and chemistry, under the circumstances, do not call for treatment here.

Zinc white, ZnO, is rarely used as a sole base, though like the lead compounds it is used 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, as for some reason, when it is 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 its presence, from 2 to 6 per cent., saves considerable colour.

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

Chalk, or calcium carbonate, $CaCO_3$, 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, as it is very sensitive 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 with pulp, but it is not a base to recommend.

Kieselguhr, a finely divided infusorial silicious earth, largely used in the manufacture of dynamite, is used with the heavier bases to make the lake lighter, and more especially in pulp colours where such bases as barytes and blanc-fixe are used, which retain but little moisture, as it 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 body is used with some basic colours, as they are absorbed and partially fixed by it. It is useful for the production of cheap deep tints, but the pigments are not of a good class; their fastness to light and moisture, and their bleeding propensities, put them at a great discount for many purposes where they would otherwise be adopted.

Aluminium hydrate, $Al_2(OH)_6$, is rarely used but freshly prepared, and the preparation is usually effected by precipitating it from the solution of a soluble salt, usually sulphate of aluminium, by sodium hydrate or carbonate. The carbonate is generally employed. The reaction which takes place can be expressed as follows:—

$$Al_2(SO_4)_3 + Na_2CO_3 + H_2O = Al_2(SO_4)_2(OH)_2 + Na_2SO_4 + CO_2$$
$$Al_2(SO_4)_2(OH)_2 + Na_2CO_3 + H_2O = Al_2SO_4(OH)_4 + Na_2SO_4 + CO_2$$
$$Al_2(SO_4)(OH)_4 + Na_2CO_3 + H_2O = Al_2(OH)_6 + Na_2SO_4 + CO_2$$

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

Sodium hydrate is very rarely used to effect this precipitation, as aluminium hydrate acts likes a weak acid with strong bases forming aluminate, and in consequence is soluble easily in an excess of sodium hydrate.

The precipitation of aluminium hydrate effected by sodium carbonate in dilute solutions is very gelatinous and possesses little or no body, but in this state possesses a considerably greater attraction for hydroxy colouring-matter than when precipitated from concentrated solutions when the precipitate is more granular; if the solutions are too strong, it forms a jelly-like mass, which is of little or no use.

Aluminium hydrate is used pretty largely for certain classes of colours which can hardly be termed true lakes. As the colouring-matter is but partially fixed by the aluminium hydrate, there is always a large loss of colouring-matter, but in the case of such things 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 taken advantage of.

It is mainly 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, and does away with the stiffness and hardness of the pulp, and owing to its gelatinous nature retains much water; it does not give alone a pigment with much value, as there is a want of body and opacity.

The method used to prepare the mixtures of aluminium hydrate and the other bases is to suspend a base like China clay in a solution of aluminium sulphate, and while vigorously agitating the mixture to slowly add 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 it is used to assist in the fixing of the colour, and 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, satin white, 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 readily combine 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, As_2O_3, 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 the precipitation; therefore it is essential to arrange that the mother liquor of the mixture should have an almost neutral but if anything slightly acid reaction, for if it be but slightly alkaline, in some cases after the colour is used and exposed to air it deepens, throwing the shade all wrong. The presence of a small quantity of sodium acetate, itself a salt with an alkaline reaction, partially neutralises the acid effect of a very slight excess of aluminium sulphate, and produces a better and more pleasing result. Reference to Plate No. 2 (opposite this page) will show—

1. An acid precipitation.
2. An alkaline precipitation.
3. A slightly acid precipitation in the presence of sodium acetate.

It may be pointed out that when a solution of sodium acetate is mixed with a solution of aluminium sulphate, a proportional 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, much feebler action on the precipitate.

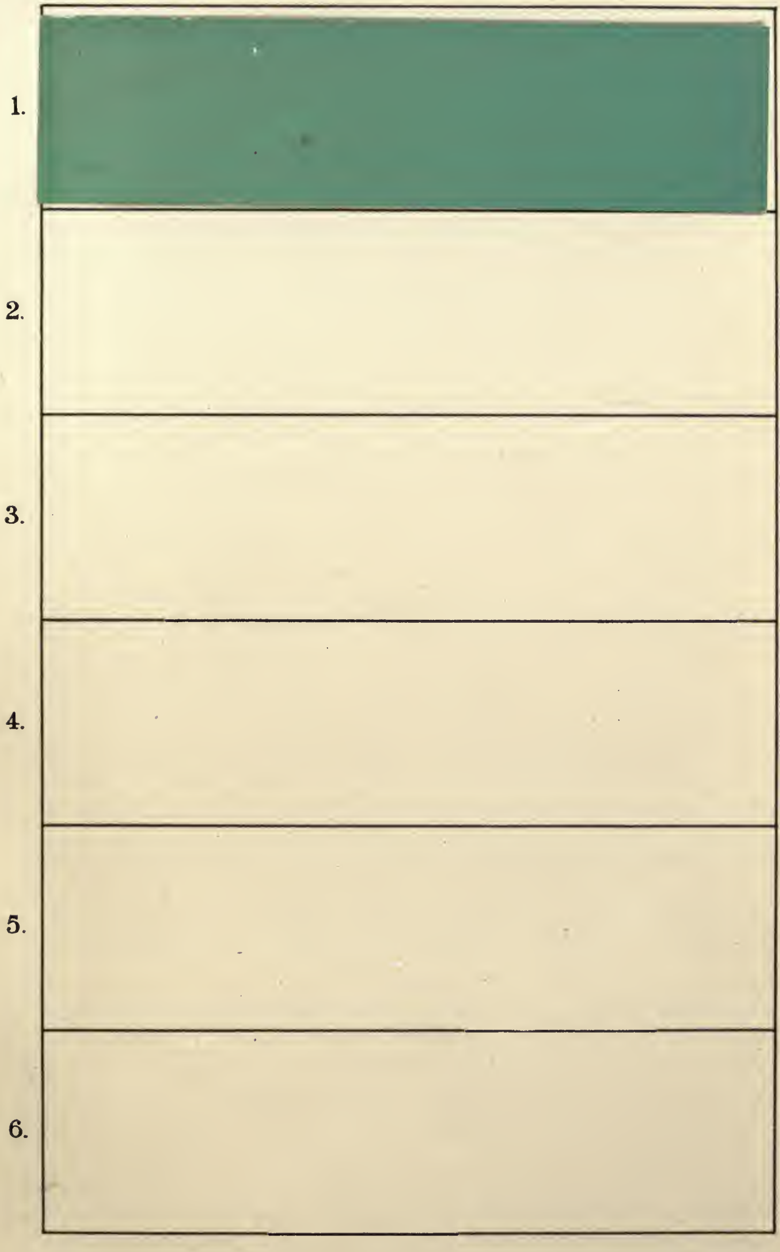
Phosphoric acid, as pointed out in a previous chapter, is especially adapted for the precipitation of the violet basic colours, and certainly the violet lakes yielded by it are very bright, and the more so when they are produced on a base of phosphate of aluminium.

The most usual method of procedure is to mix the solutions of the colour or colour with a solution of aluminium sulphate, and then 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:—

$$Al_2(SO_4)_3 + 2Na_2HPO_4 + Na_2CO_3 = Al_2(PO_4)_2 + 3Na_2SO_4 + H_2O + CO_2$$

If the solution be either acid or alkaline, there is sure to be

PLATE II.



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 are used, the pigment is pervaded with small white lumps, and if solutions are too weak or too cold the lake has no body, and retains far too much moisture, besides being difficult to handle.

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 matching a particular shade, as 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. Without entering into elaborate details concerning the combination of the two methods, the following examples 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 aluminium sulphate solution containing the clay, the aluminium hydrate formed is more thoroughly incorporated with it than it would be by any merely mechanical admixture. 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 decomposition of the aluminium sulphate, forming 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 which often, on the addition of the colour, partially combines with it as well, as is natural to it, absorbing the colour; 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 the thoroughly incorporated mixture produced by the reaction of the colour, barium chloride and sodium sulphate.

The 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 carefully examine the colour, and devise for himself the most rational way to produce the best result, and, by adopting those bases which he knows from experience to be most suitable for the purpose the pigment is required, to experiment until he arrives at the most satisfactory result; for 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.

PLATE III.

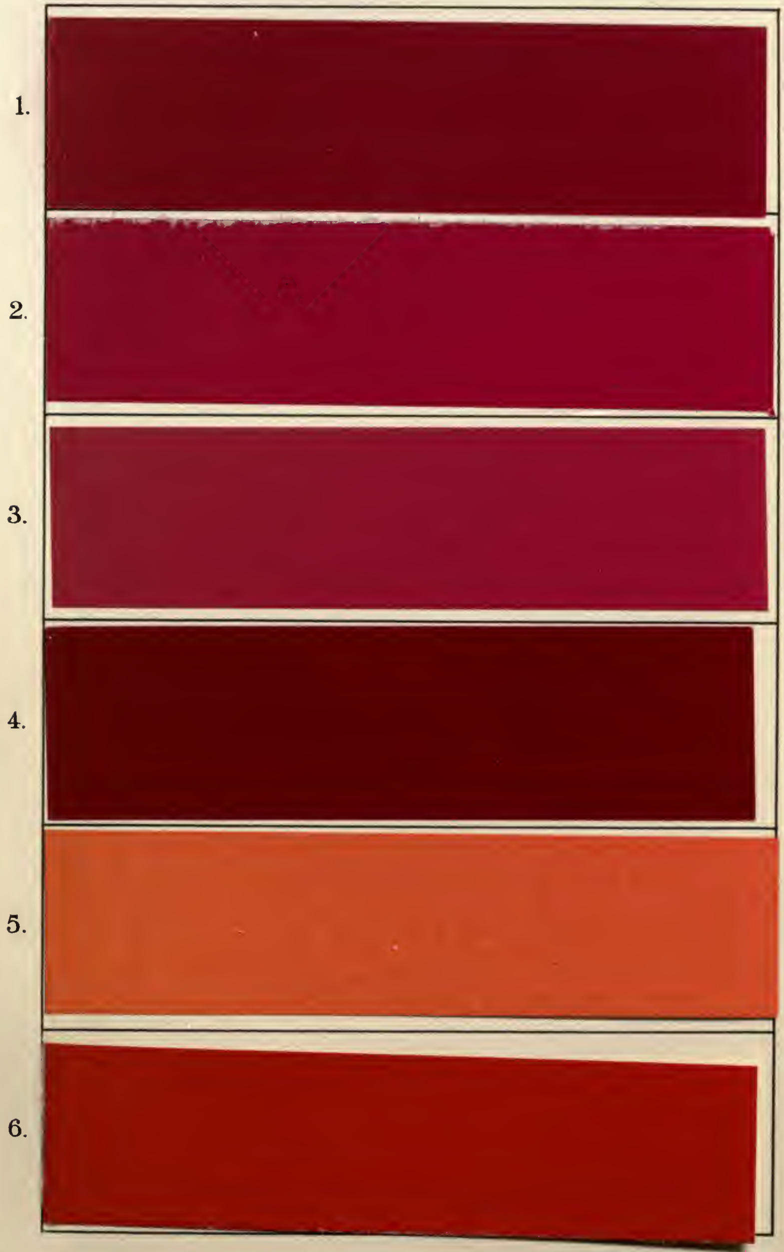


Plate No. 3 (opposite this page) shows—

1. 5 per cent. eosine A, on barytes, precipitated by lead acetate.
5 ,, ,, on blanc-fixe.
5 ,, ,, on clay.
5 ,, ,, on barytes and kieselguhr.
10 ,, barium lake of brilliant orange R on blanc-fixe.
10 ,, ,, ,, ,, precipitated on a clay and alumina lake, simultaneous with the production of blanc-fixe.

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 this 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 the 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 three classes—

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

The basic colours are those containing amido 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 negligeable from a lake-form 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 therefore necessary to carefully consider the method of procedure which should be followed where the lake-forming group or groups in a colouring-matter are of a simple nature, and from which simple lakes can readily be formed, and in those of a more complex constitution containing several groups, which only give satisfactory results 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; but a lake pigment must be regarded as the chemical combination of the dyestuff with one or more bodies, which confer on it the pigmentary qualities, 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, and that the reactions can be expressed by simple chemical equations, is a very moot point; though in some cases experimental data indicate such simple changes, 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, green earth, 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 owing 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 to be remarked in the case of weak bases combined with weak acids. Though the cause for 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, as well as prompts one to condemn entirely such methods of producing such mixtures 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 to what 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 barely to be conceived 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 used; and for the greater brightness, the plan of using but the necessary quantity of tannic acid in these cases has obtained for the tannic acid lakes a reputation for being far more fugitive than they really are, and causes them to be ranked but little faster than the fugitive lakes produced by such acids as arsenious and phosphoric, when they are really the most permanent of any 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 the lake-forming groups are combined with those bodies for which they have an affinity.

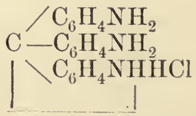
An example is shown on Plate No. 4 (facing page 78), in which No. 1 is the barium lake on an aluminium hydrate and blanc-fixe base of concentrated acid green D (M. L. & B.), a colour which yields fairly fast green lakes. The precipitation is almost complete with barium chloride; but if, previous to the addition of the chloride of barium, tannic acid be added to the colour, a much brighter and faster pigment is formed, which is shown by No. 2. The increase 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. This reagent has not the power 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 dyestuff.

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, which ensures there being an excess of the precipitating body present, as the reaction is brought about by precipitating the insoluble metallic salt, together with the insoluble salt of the colouring-matter, and therefore 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, which has already been gone into.

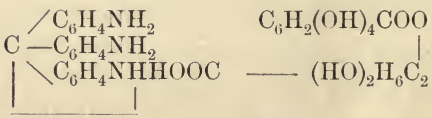
The most permanent lakes produced from basic colours are the tannic acid lakes, which though duller, even when correctly prepared, are much more permanent than the lakes produced from these colours by other means; but the tannic acid lake produced, say, from a magenta salt, *e.g.* the hydrochloride—



$$C\begin{cases} C_6H_4NH_2 \\ C_6H_4NH_2 \\ C_6H_4NHHCl \end{cases}$$

when converted into

the tannate gives—



$$C\begin{cases} C_6H_4NH_2 \\ C_6H_4NH_2 \\ C_6H_4NHHOOC - (HO)_2H_6C_2 \end{cases} \quad C_6H_2(OH)_4COO$$

This salt is soluble in the hydrochloric acid liberated, and though almost complete precipitation is obtained if an excess of acetate of soda be first 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, owing to being a tartrate, is able itself to combine with the basic colouring-matter, but in few instances gives precipitates that are not soluble in hot water, and 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, which, though not as bright as the arsenious acid lakes, is much brighter and far more permanent than those produced from tannic acid or tannate of soda.

To practically and readily determine the exact amount of tannic acid to use 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, which its physical behaviour increases. Where the theoretical amount is used, a much faster though at the same time duller lake is produced, therefore 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. Where the constitution and the purity of the colour being employed is approximately used, 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 is 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, as if, previous to the addition of tannic acid, this proportion of tartar emetic is 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, in which case the injurious effects produced by an excess of these reagents is reduced to a minimum, for what tannic acid and tartar emetic are 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-matter and the two lake-forming bodies should be maintained.

The results obtained by precipitating basic colours in various ways is illustrated on Plate No. 4 (opposite this page), where—

Sample No. 3. Arsenious acid precipitation of rubin small crystals.
,, ,, 4. Tannic ,, ,, to complete precipitation.
,, ,, 5. ,, ,, ,, theoretical quantity.
,, ,, 6. ,, ,, and tartar emetic precipitation, theoretical quantities.

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 taken advantage of in tinting colours to various shades, and though perhaps the result of such combinations lead 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, and it is far the

PLATE IV.

best, where it be practicable, to combine each colour with its typical lake-forming compound.

Of the acid colours, the nitro derivatives are perhaps the least used of any, because their metallic salts are usually extremely soluble, and those of the few combinations with the oxides of the heavier metals are not of such a nature 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 the value of it as a lake-forming group is not great in the monohydroxy compounds, but in those where it occurs as a dihydroxy derivative.

The position of the hydroxy groups in the molecule is of considerable influence on the lake-forming properties, for unless the hydroxy groups be in the ortho-position as regards each other, the lakes produced are not fast, but may be reckoned among the most fugitive, as for instance the eosines, which are metahydroxy compounds; and again the alizarines, which are orthohydroxy compounds, yield the fastest of all the lakes.

The lake-forming bodies for the orthohydroxy bodies 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 ocid 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 as regards themselves or the carboxyl group, they possess the same properties as regards lake-formation as the diortho-hydroxy 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 the properties similar to those of the alizarines.

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

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

The increase in the number of sulphonic acid groups in a molecule of a colour does not increase its lake-forming power, and the position of the sulphonic acid in the colour molecule has a very considerable influence on the lake-forming capacity; for similar compounds prepared on the same lines, but with the sulphonic acid in different positions, show marked difference in their behaviour with lake-forming bodies; and it must be concluded that 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, and this 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 gone into, so that the constitution of the sulphonated dyestuffs used in lake-making should be carefully examined, and its behaviour with precipitating agents, and its 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 be not in the ortho-position as regards 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 take the full development of the chromatic power of the colouring-matter; and as aluminium and allied oxides and hydrates are the lake-forming bodies for these groups, the aluminium barium lake must be prepared, the combination of one instead of both the lake-forming groups of the colouring-matter must be effected, otherwise the result is usually useless for pigmentary processes.

Although the lake formation in other than those dyes 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, but it will be found that the stronger the basic properties of the sulphonated base are, the more difficult it is to produce simple barium lakes from them, though in all cases 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.

By 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, the basicity 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, also 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, not 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 hydrate 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 capability of the basic group will have disappeared; therefore, after the formation of the barium lake, the dyestuff may be regarded as an ortho-hydroxy-carboxyl compound, and the compound lake produced by the means already entered into for such compounds.

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. Of the basic dyes they belong principally to—

I. The triphenyl-methane colours, of which magenta and rhodamine are typical examples.
II. The azines, which is 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 not only is used alone to form lakes of a magenta-red shade, but with acid scarlets and reds to produce various shades of red. It is not much use in modifying the shade of violet lakes, as its pronounced shade interferes with the shade of the mixed colour lake, giving 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 crystallised 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 productions 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 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, *i.e.* the rhodamines, are largely used for tinting violets; they are then precipitated with phosphoric acid or its salts. They are not very powerful colours; a very small percentage in the mixed colouring-matters of a strong colour like methyl-violet B is sufficient to give the shade of violet to the lake.

Plate No. 5 (opposite this page) shows the tartar emetic and tannic acid lakes of these rhodamines :—

1. 2 per cent. lake rhodamine B extra.
2. 2 ,, ,, ,, 6G extra.
3. 10 ,, ,, ,, 12G.

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

The only lakes which are at all to be recommended of the safranines are the tartar emetic and tannic acid lakes. 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, as 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.

On Plate No. 5, also, will be seen the—

4. Tartar and tannic lake of safranine YOOO (Basle), 5 per cent.
5. ,, ,, safranine YOOO, and lead lake of eosine A (B.A.S.F.).
6. Tartar and tannic acid lake of rhodamine B, and lead lake of eosine A (B.A.S.F.).

With the safranines, as well as all other tannic acid and tartar emetic lakes, the most suitable base is blanc-fixe.

The red colouring-matters of the azo group are very great, and the number at the disposal of the lake-maker often causes the use of a very large number of brands, and often causes considerable hesitancy before selecting what

PLATE V.

colours should 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 to produce it from. Almost all shades of red and maroon produced from this colour can be obtained from a range of four to eight shades of colour, *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.

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 are much more easily converted into pigments, and are as a rule much cheaper.

When using hydroxy-sulphonic acid colours, the best base to use is one containing aluminium hydrate, as the shades produced are much clearer and brighter when this body is present, for 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, as it is then thoroughly incorporated with them, and a homogeneous base is the result.

The precipitating agent to be used for the greater 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 they are more readily changed by the action of air and light.

The best methods of producing pigments from this class of red dyestuffs is to precipitate them simultaneously with barium sulphate or blanc-fixe, on a freshly prepared aluminium base, by means of barium chloride.

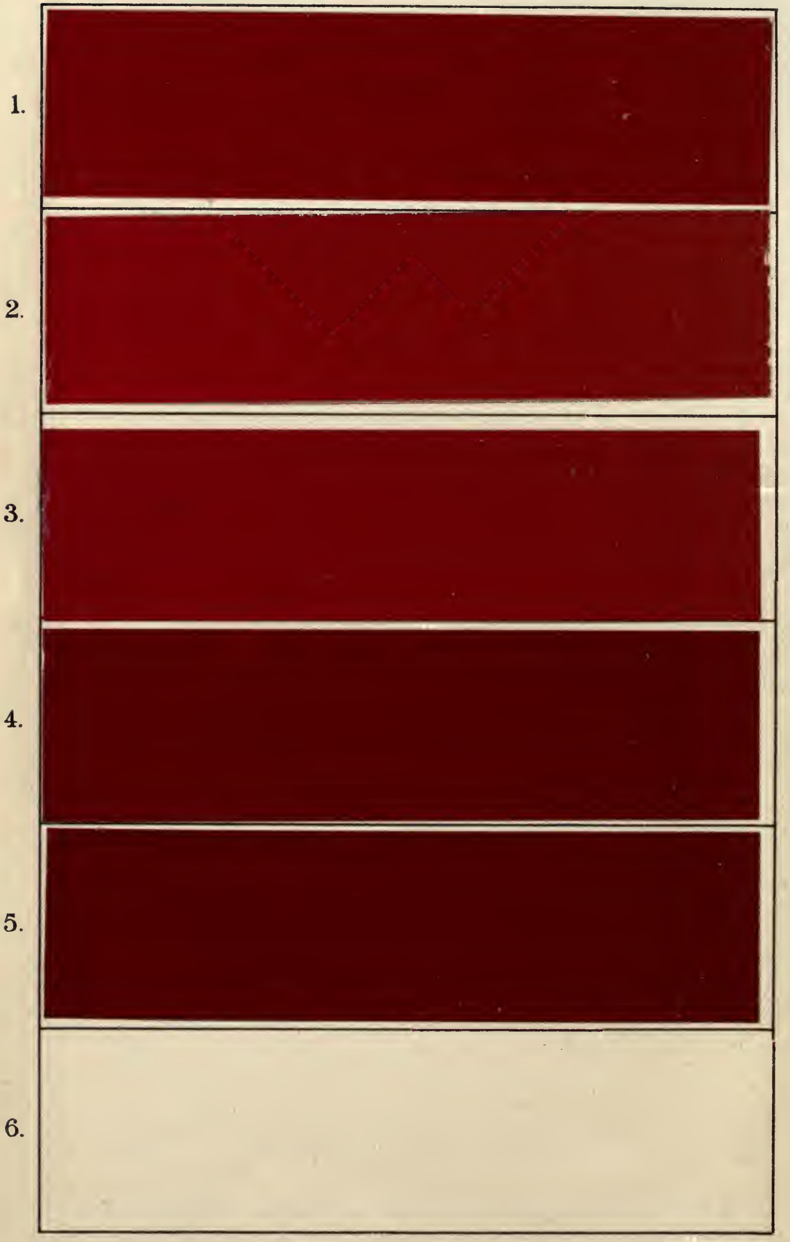
Plate No. 6 (opposite this page) shows a series of shades produced from three brands of scarlet:—

No. 1. Ponceau GL (Ber.), precipitated on an aluminium hydrate base, simultaneous with the production of blanc-fixe, by means of barium choride.
,, 2. Scarlet 3R (M. L. & B.), similarly produced to No. 1.
,, 3. Ponceau 4R, produced in a similar manner to Nos. 1 and 2.
,, 4. Ponceau GL, precipitated on blanc-fixe by means of barium chloride.
,, 5. Scarlet 3R (M. L. & B.), precipitated on blanc-fixe by acetate of lead.
,, 6. Ponceau 4R (Ber.), produced in a similar manner to No. 3, but with barytes in the base, together with the aluminium hydrate.

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

PLATE VI.

PLATE VII.



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.

These points will be found illustrated by Plate No. 7 (opposite this page), in which—

No. 1. Lake made from scarlet GR (Ber.), clay aluminium hydrate base, precipitated by barium chloride.
,, 2. Lake made from scarlet GR (Ber.), and orange II (Basle), 10 per cent. of the total colour used being orange II on the same base as No. 1, and precipitated in the same way, the colours being dissolved together.
,, 3. Same as No. 2, but colours dissolved separately.
,, 4. Scarlet GR, scarlet 3R, fast red O, on alumina base, precipitated together with blanc-fixe by barium chloride, the colours dissolved together.
,, 5. Same as No. 4, but colours dissolved separately.

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 of 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 to always use a proportion of bright scarlets in the mixture used for the production of maroons.

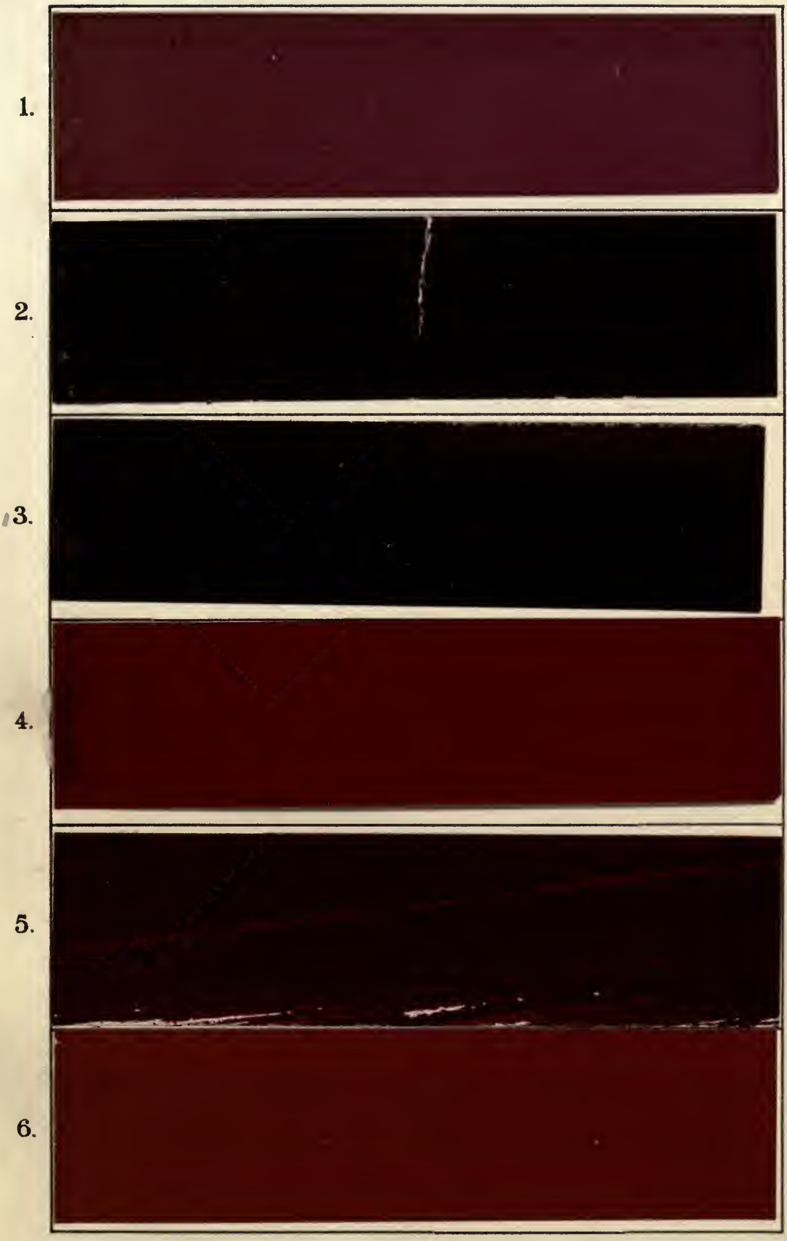
Maroon shades, made by means of the property of acid colours to combine with basic colours, are much more fugitive than those in which the basic colour is introduced in the form of a pigment, and, as mentioned before, they have a tendency when dried at 100° C. to turn much deeper and blacker, losing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

The action of the various basic colours mentioned is shown in Plate No. 8 (opposite this page), in which—

No. 1. Maroon, produced from fast red O (M. L. & B.) and rubin small crystals (in form of 10 per cent. tartar and tannin lake on clay).
,, 2. Maroon, produced from equal parts of fast red O (M. L. & B.) and scarlet 3R (M.L. & B.), pigment magenta, as in previous case.
,, 3. Maroon, from scarlet 3R and magenta, the rubin small crystals (Ber.) being carried down by the scarlet 3R.
,, 4. Similar to No. 3, but pigment magenta used.
,, 5. Similar to No. 3, but pigment of safranine YOOO used.
,, 6. Similar to No. 3, but pigment Bismarck brown used.

The acid red colouring-matters of the triphenyl-methane colours are comprised mainly of the eosines and allied colours. They are hydroxy colours. The hydroxy groups are not in the ortho-position as regards 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

PLATE VIII.



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. They, *i.e.* the eosines, etc., all contain a large number of halogen atoms in their constitution, which probably largely influences the attraction of the compounds 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.), as will be seen in Plate No. 9 (facing page 92), where—

No. 1 is a 5 per cent. lake of eosine A, and
,, 2 is a 5 per cent. lake of eosine yellowish,

yet both are salts of tetrabrom-fluoresceine.

Rose Bengale 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; but 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 out together. In this case there is no advantage to be gained by using a pigment of rhodamine, as 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 vermilionettes and similar colours used largely for paint; they are for this purpose 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 really suitable one; but mixed aluminium hydrate bases are largely used when aluminium and tin are used as precipitating agents. The samples on Plate No. 9 (opposite this page), from Nos. 3 to 6, show the various shades produced from the same eosine by various precipitating agents:—

No. 3. Eosine A (B.A.S.F.) on blanc-fixe, precipitated by lead acetate.
,, 4. Eosine A and rhodamine B on blanc-fixe, precipitated by lead acetate.
,, 5. Eosine on blanc-fixe, precipitated by zinc sulphate.
,, 6. Eosine on blanc-fixe, precipitated by aluminium sulphate.

The selection of the brand of eosine to use is a matter of some difficulty, as 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 the most fugitive lakes it is now necessary to pass to the consider-

PLATE IX.

ation 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, cœrulein, 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 purposed to go into the details of these methods, but to give an outline of the most essential points to be observed in the 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; but which 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 similar bodies must be present. What the exact composition of the lake is, cannot be accurately stated.

The red alizarine colours yield with aluminium, red or scarlet lakes; with iron, browns; and chromium, maroon shades. The brilliant shade of the aluminium lakes is at once destroyed should there be present in it but traces of iron. In the satisfactory production of lakes from alizarine colours, too much attention cannot be paid to the purity of the chemicals used; further time must be allowed for the lake formation, for the more slowly it is brought about the better and brighter the results.

Most of the alizarine colours are insoluble in water, but soluble in alkaline solutions. 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 very slowly in, the evolution of carbon dioxide never being allowed to get very 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 risen 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 the 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.

The part played by the phosphoric acid is rather obscure, for it appears in the lake, and, if the process be carried out without it, no satisfactory result can be obtained on a large scale.

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-works rather lack body, but are used for tinting purposes, yielding when reduced shades very similar to those produced by eosine, but 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 for this reason. The following

PLATE X.

plate, No. 10 (opposite this page), illustrates a few points concerning alizarine lakes:—

No. 1. Aluminium lake from alizarine (No. 1 B., new, M. L. & B.), made very slowly.
,, 2. Same as No. 1, made quickly.
,, 3. Same as No. 1, but contaminated with iron.
,, 4. Aluminium alizarine lake, reduced with white.
,, 5. Eosine lake, reduced with white.

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, as to whether it be an acid or a basic colour, and the process for converting it into a lake pigment devised accordingly.

Orange lakes are principally manufactured from azo-sulphonic acids, as they yield much fuller and brighter colours than the basic oranges, such as the phosphines.

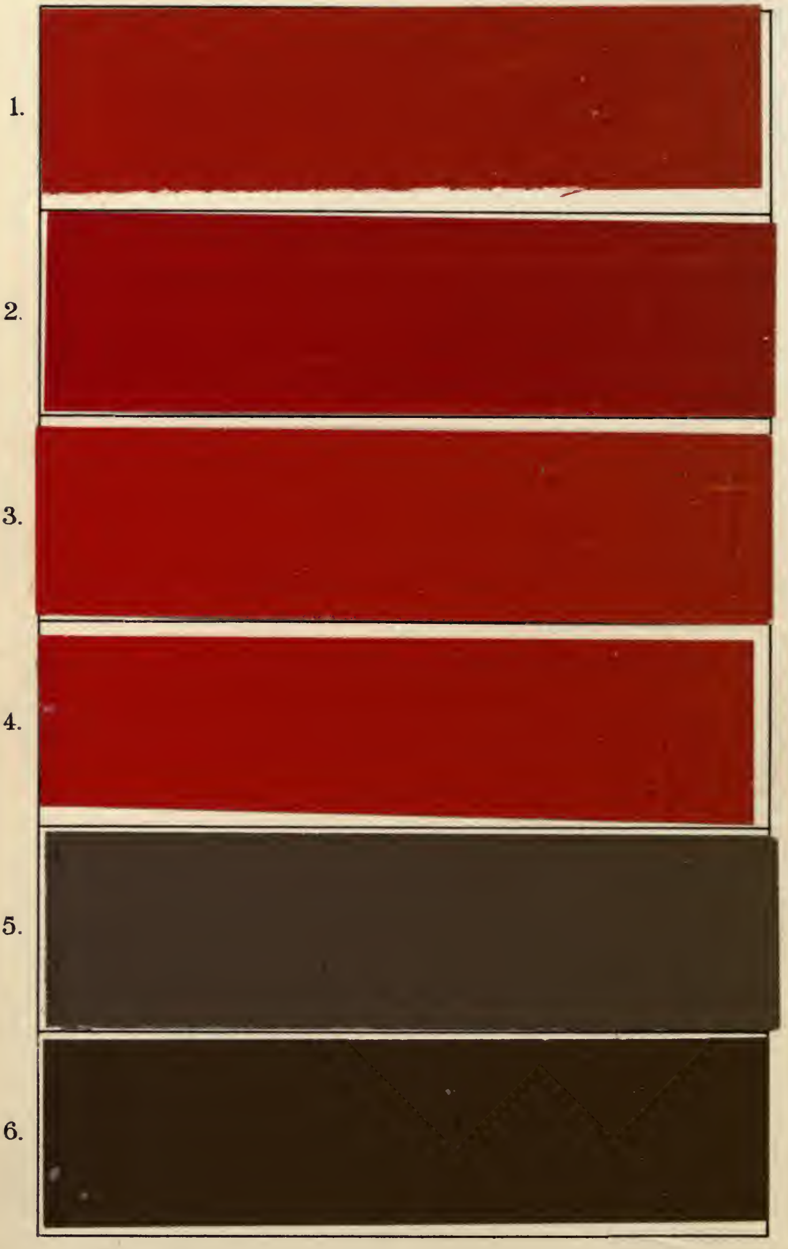
Nitro-alizarine, or alizarine orange, is not used in the production of lake pigments, as the presence of the nitro group interferes with the ordinary methods used in the production of alizarine lakes.

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 concerning the selection of azo-scarlets.

The precipitating or lake-forming agent is therefore 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) yield clear bright lakes. The extra qualities of the brilliant

PLATE XI.



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, however, so made are not very fast, and soon fade.

Plate No. 11 (opposite this page) illustrates the difference in shade of some brands of orange:—

No. 1. Mandarin R, on alumina and clay.
,, 2. ,, on barytes.
,, 3. Orange II (Basle), on alumina and clay.
,, 4. Brilliant orange R, on alumina and clay.

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 albumen is run into the cold preparation and the temperature gradually raised to the boil.

The samples Nos. 5 and 6 on Plate No. 11 (opposite this page) show a lake made from acid brown B (Basle) on blanc-fixe. In No. 5 the precipitation is brought about by barium chloride; in No. 6, after the addition of the barium chloride, tartar emetic is added to the tank, and the precipitation completed by the addition of tannic acid. The supernatant liquors in the latter case are very clear; in the former they are heavily charged with colouring-matters.

Yellow lakes are very rarely manufactured, because the chrome yellows are not only much faster but much cheaper. 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 thiobenyl colour. There are numerous acid yellows, of which naphthol yellow S, metanil yellow, quinoline yellow, and tartrazine, a hydrazine colour, are the most useful of them for lake production.

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, as it yields only fugitive shades, which on drying or standing in the pulp state, after washing dissociate, giving the lake a mottled yellow appearance.

Where purely basic greens are used, or where the pigment is formed by methods for the precipitation of basic colours only, the basic yellows, auramine or thioflavine T (C.), should be used. The influence of the yellow used on the shade produced is well illustrated on Plate No. 12 (opposite this page), where in No. 1 the pure shade green produced by thioflavine T is contrasted with the myrtle shade produced by auramine in No. 2. This difference holds good whether the lake formation be due to arsenious, tannic, or other acid.

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 is to be preferred, as it gives more delicate tints, as will be seen on comparing Nos. 3 and 4 on Plate No. 12 (opposite this page). In No. 3, acid green D (Conc.), M. L. & B., is tinted with

PLATE XII.

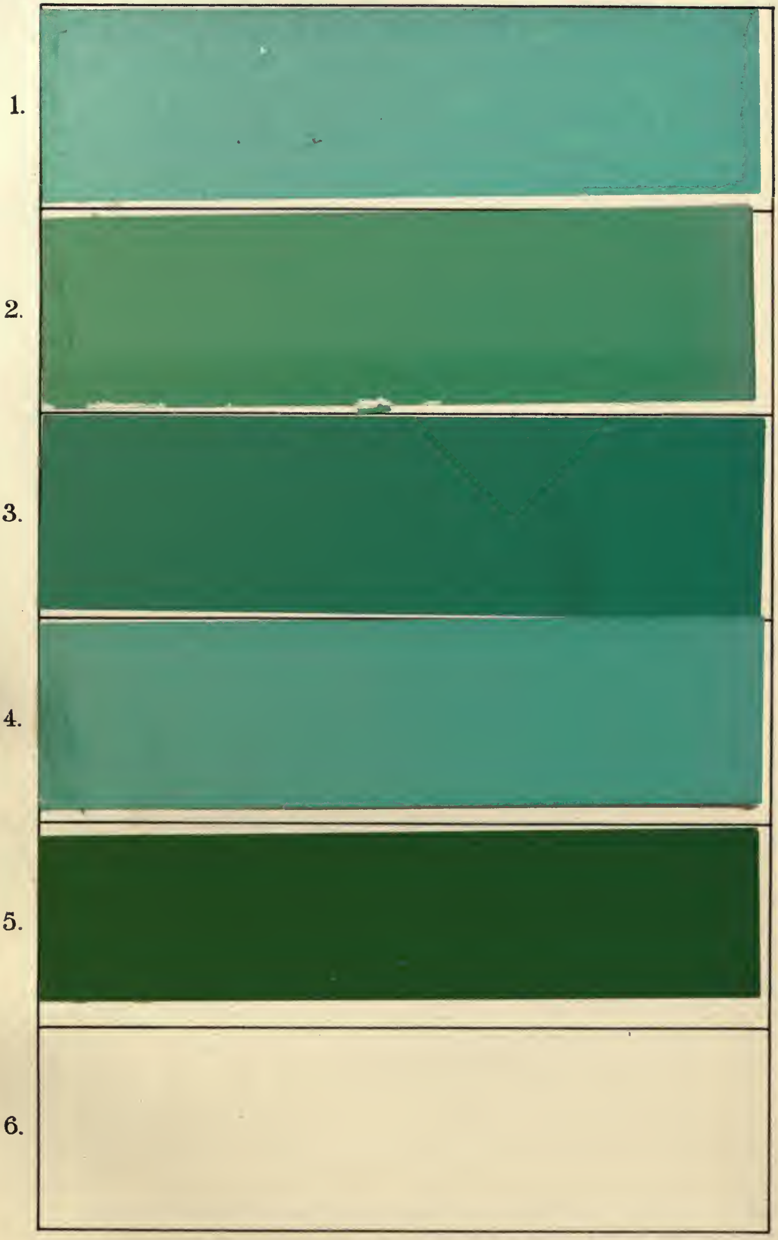
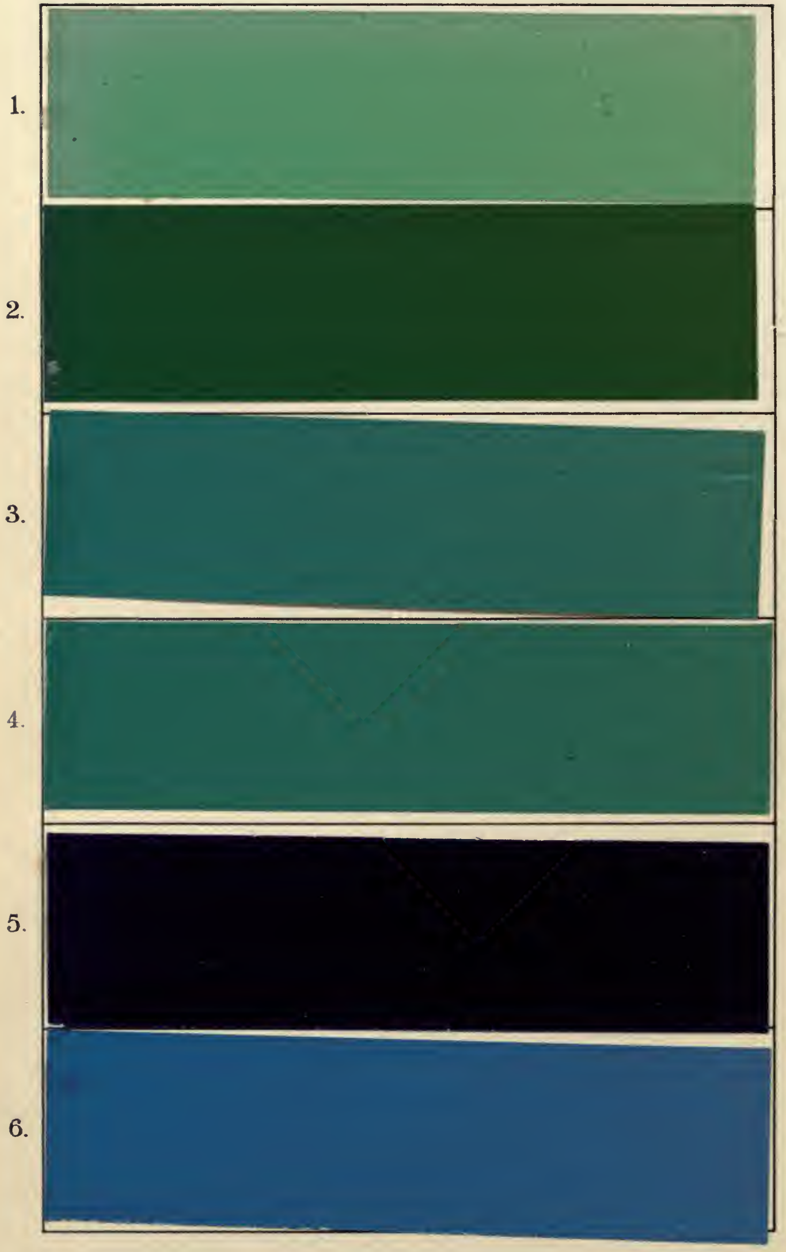


PLATE XIII.



naphthol yellow S, and in No. 4 with quinoline yellow (Ber.). Metanil yellow works well with greens used to produce the double barium and tannic acid lakes, as it contains an amido group; it yields sage-green tones of a peculiar cast, which reference to No. 5 on Plate No. 12 (facing page 98) will show.

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, as will be seen by referring to Plate No. 13 (opposite this page), in which No 1 is the arsenious acid lake of ethyl green and auramine, and No. 2 is the same colours put down on blanc-fixe by tartar emetic and blanc-fixe.

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. This is shown on Plate No. 13 (opposite this page), in samples Nos. 3 and 4, the first being simply the barium lake of acid green D (Conc.), M. L. & B., and naphthol yellow S, and No. 4 the same lake only treated with tartar emetic and tannic acid after the precipitation by barium chloride.

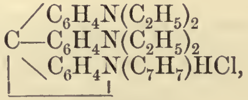
There is very little to choose between the brands of the various purely basic greens in the market. Preference, if any, might be given to the ethyl-green crystals (Ber.), the brilliant green of (C.), and the diamond greens of B.A.S.F. Of the acid greens, of the many that the author has examined, the 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, as the process that must be adopted is similar to that used to produce lakes from alizarine and allied colours.

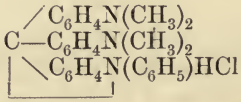
Blue lakes for certain shades are largely used, but as they are derived from basic or sulphonated basic colours, they are rather fugitive, and mineral pigments, such as the ultramarines and the ferrocyanide compounds of iron, are preferred to them.

The colours from which they are derived belong chiefly to the triphenyl-methane group, the oxazine 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 yields full deep blues of rather a reddish tone. The purely basic blues of the triphenyl-methane group can be typically represented by—

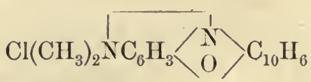
Nile blue,


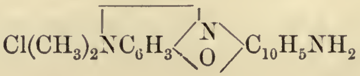
$$C\begin{array}{l}\diagup C_6H_4N(C_2H_5)_2\\ —C_6H_4N(C_2H_5)_2\\ \diagdown C_6H_4N(C_7H_7)HCl,\end{array}$$

and Victoria blue,


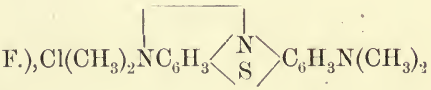
$$C\begin{array}{l}\diagup C_6H_4N(CH_3)_2\\ —C_6H_4N(CH_3)_2\\ \diagdown C_6H_4N(C_6H_5)HCl\end{array}$$

The oxazines and thiazines by—

Naphthalene-blue R (By.),


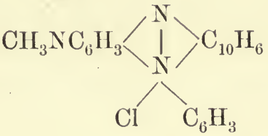
Nile blue A (By.),


Methylene-blue B (B.A.S.F.),



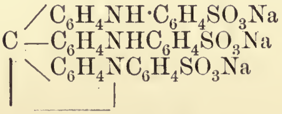
The indulines by—

Neutral blue (C.),

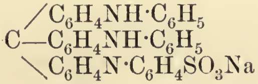


With tartar emetic and tannic acid on clay or blanc-fixe, these colours yield full deep fine shades of blue of a pleasing tone, but they all more or less tend to the red side. To obtain pure blue shades, it is necessary to use the acid blues, *i.e.* the sulphonated basic blues, which belong mainly to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

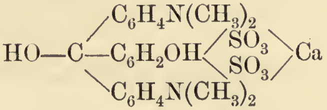
Diphenylamine blue,



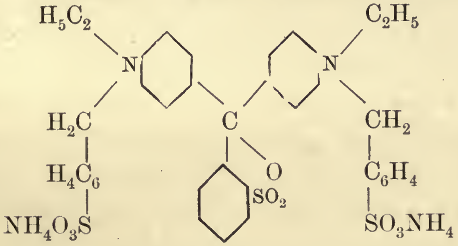
Alkali blue D (Ber.),



Patent blue BN (C.),



The erioglaucine blues of Geigy, derivatives of—



The latter two are rather difficult to precipitate. In the case of patent blue BN a satisfactory precipitate is not obtained if, as well as tartaric emetic and tannic acid, barium hydrate is not 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, or complete precipitation is not attained. The shade produced from erioglaucine A is a very pure azure blue. In Plate No. 12 (facing page 98), sample No. 5 shows the general style of blue obtained from a basic blue, namely, Victoria blue, with tartar emetic and tannic acid on blanc fixe; No. 6, the shade produced by erioglaucine A on a base of clay and alumina containing a little zinc hydrate.

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, as 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.

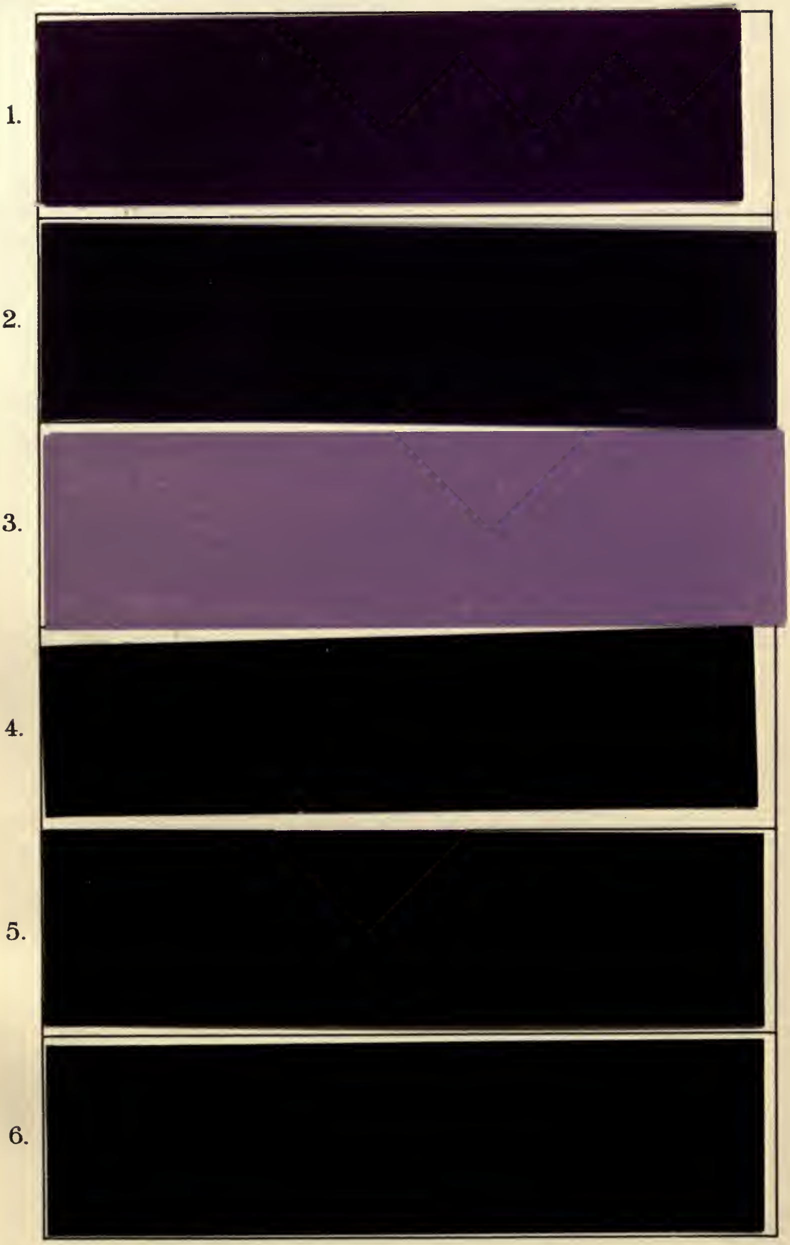
The deep blues that might be obtained from the alizarine blues have in the form of lakes little or no market, and are therefore not manufactured.

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 amido groups must be combined with tartar emetic and tannic acid, as well as 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 comparison is shown in Plate No. 14 (opposite this page), where No. 1 is the phosphoric acid lake of methyl-violet B, and No. 2 is the tartar emetic and tannic acid lake. 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, as magenta or safranine give rather harsh shades.

The fastest violet lakes are produced from gallein in

PLATE XIV.



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. A shade given by it when reduced with white is shown in No. 3 on Plate No. 14 (facing page 102).

Black lakes are mainly produced from the azo-acid colours. They are treated in the same manner as the azo-scarlets, but as 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. On Plate No. 14 (facing page 102) is shown the lake of black (acid) F.H.A., Basle, on an aluminium base precipitated with barium chloride in No. 4, and its action in a pigment made from vegetable black is shown in Nos. 5 and 6, No. 5 being the black base on which the black is precipitated, and No. 6 shows the alteration in shade produced by the precipitation of the black.

CHAPTER X

THE PRODUCTION OF INSOLUBLE AZO COLOURS IN THE FORM OF PIGMENTS

THE introduction of primuline, and the method of dyeing ingrain colours by Green in 1887, by which the amido groups of the primuline were diazotised after dyeing on the fibre and then combined with an amine or a phenol, lead 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 diazotised 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, save primuline, the colours produced from dyes are browns, blues, and blacks, which colours produced from coal-tar products are of but little demand, and the red shade produced from diazotised primuline and β-naphthol is very little superior to that produced more easily from an ordinary azo-sulphonic acid.

These pigments are therefore produced almost entirely by diazotising 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 two principal being, first 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, 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.

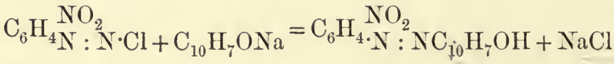
The action that takes place can be best illustrated by the production of the best known of these colours, *i.e.* paranitraniline red, which is produced by combining diazotised paranitraniline with β-naphthol.

Paranitraniline $C_6H_4\left\{\begin{matrix}NO_2\\ NH_2\end{matrix}\right.$ is a bright yellow powder of a crystalline nature, which is very slightly soluble in water, but soluble in hydrochloric acid, producing the hydrochloride which is fairly soluble in boiling water, from which unless very dilute it is precipitated on cooling; 1 to 2 per cent. solutions only do not deposit on standing. The solution has a clear yellow colour, which turns slightly browner when the nitrite of soda is added, owing to the amido group being converted into diazo group. Thus—

$$C_6H_4\left\{\begin{matrix}NO_2\\ NH_2 2HCl\end{matrix}\right. + HNO_2 = C_6H_4\overset{NO_2}{N} : N : Cl + H_2O$$

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. If there has been but a slight deposition of the paranitraniline the sodium nitrite may be added; but unless before decomposition sets in it has not entirely disappeared, it is useless to proceed, as specks of yellow will pervade the whole pigment, and the colour produced will be dull and unsatisfactory.

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



$$\overset{NO_2}{C_6H_4}N:N\cdot Cl + C_{10}H_7ONa = \overset{NO_2}{C_6H_4}\cdot N:NC_{10}H_7OH + NaCl$$

Various makers of paranitraniline give recipes for making 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, what may work well in one place does not do at all in another; it is therefore of little or no use giving proportions, etc., for the production of these pigments, as considerable practice is necessary to really obtain good results, and it is by far the best way to work out carefully with pure chemicals some recipe such as the following:—

Naphthol mixture	224	parts	blanc-fixe
	2·5	,,	$\beta C_{10}H_7OH$
	0·7	,,	NaHO
	2·5	,,	Na_2CO_3
	1·0	,,	oleine

Diazo mixture	2·4	parts	$C_6H_4NO_2NH_2$
	6·0	,,	HCl 1·2 sp. g.
	1·22	,,	$NaNO_3$
	250	,,	water

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

Having obtained a satisfactory shade from pure chemicals, a careful comparison should be made and noted between the pure and commercial materials, and on this comparison to devise suitable working proportions, suitable to the quantities it is desirous to make and appliances at hand; for these colours are easily made when attention is carefully paid to detail, and these details cannot be pointed out, as 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 that are made in the course of the operation.

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

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

They are often sold under the name of developers, and are then usually prepared for use by being combined with sodium in the case of phenols, and as salts in case of the amines.

Among the chief bases that are diazotised are—

m. and p.-nitraniline.
p.-phenilidine sulphate.
o.-nitro-p.-phenilidine.
The various azophor reds, etc.

CHAPTER XI

THE GENERAL PROPERTIES OF LAKES PRODUCED FROM ARTIFICIAL COLOURS

PIGMENTS produced from artificial colourings are, save those obtained from alizarine, its allies, and those obtained by producing azo colours, by combining a diazotised amine with a naphthol or an amine, are not fast to exposure to light, air, and moisture; some are much faster than others, 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, the triphenyl-methane basic colours, such as ethyl and methyl green, magenta, Nile blue, etc., which six hours' exposure is sufficient to greatly alter. 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, or they would largely displace the arsenious lakes of magenta, the shade of which they approximate.

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

PLATE XV.

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

and were exposed to the action of light, air, and moisture. At the end of three days

(1) had faded to a dirty brown,
(2) and (3) had but lost a little brilliancy.

It took about ten days' exposure to fade them to the hue given by (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; in the case of oranges and yellows, becoming dirty and brownish; scarlets, crimsons, cardinals, darkening and becoming much bluer; magentas, violets, maroons, blacken with an entire change in shade; greens become bluer, and bleach with great rapidity.

The covering and staining power of the pigments is dependent on the base used and colour the lake is made from. The pigments made from basic colours, such as Bismarck brown and magenta, have as a general rule much greater staining power than those produced from sulphonic acid colours, as will be seen in Plate No. 15 (opposite this page), in which—

No. 1 is a 5 per cent. eosine lake.
,, 2 is a 5 per cent. eosine lake, reduced 1 part of lake to 20 of enamel white.
,, 3 is a 5 per cent. magenta lake.
,, 4 is a 5 per cent. magenta lake, reduced 1 part of lake to 20 of enamel white.
,, 5 is a 5 per cent. ponceau lake.
,, 6 is a 5 per cent. ponceau lake, reduced 1 part of lake to 20 of enamel white.

By a 5 per cent. lake is meant one in which there is 5 per cent. of pure lake in 100 of dry pigment.

Plate No. 15 (facing page 109) was prepared from the 40 per cent. pulps of such lakes, and a 60 per cent. enamel white paste.

Alizarine lakes possess great staining power, which is shown in Plate No. 10 (facing page 95), in which—

No. 1 is an alizarine lake.
„ 4 is the same lake, reduced 1 part of lake to 50 of enamel white.

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. But it must be borne in mind that though a lake may be matched to work in size, it is not a match when worked in other media; for 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.

The density and fulness of a lake pigment is entirely dependent on the base being suitable for the production of the lake of a given colour and the precipitating agent used, and it is only by repeated trials and comparisons that the most suitable and economical method can be obtained from a given colour or series of colours.

Dry lakes should not be hard, or in any way horny, as this indicates that too much colouring-matter has been used, but should be very friable, and when worked in oil should not stick or lump together, but should readily mix with the oil or lithographic ink.

There can be no fixed percentage for dry colour in pulp

PLATE XVI.

colours set down, for the difference in the property of containing water in the various classes of lakes is very great; but it should always be arranged that if a lake gives satisfaction, when containing a certain percentage of dry pigment, it should always be maintained at that percentage, for if it be sent out containing more than the usual percentage it will not be usable, because it will not fall down and work easily in the size, and if containing a greater proportion of water, it will work far too thin. This is illustrated by the samples shown in Plate No. 16 (facing this page):—

I. 45 per cent. (dry colour) pulp pigment, in half its weight of prepared size,
II. 60 per cent. (dry colour) pulp pigment, in half its weight of prepared size,
III. 60 per cent. (dry colour) pulp pigment, in an equal weight of prepared size,
IV. 30 per cent. (dry colour) pulp pigment, in half its weight of prepared size,
V. 30 per cent. (dry colour) pulp pigment, in quarter its weight of prepared size,

the colour used being the same make of an ordinary scarlet. A rough method of testing whether a pulp pigment is in proper condition is by putting a couple of ounces of it in a vessel with about an ounce of prepared size, and stirring it gently with a stick or glass rod. If the lake has been properly made and in proper condition, it will be found that it will with very little agitation form a creamy homogeneous mixture with the size.

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

The solubility of a lake in water has certain drawbacks, among which is the fact that such a colour cannot be completely precipitated, leading to a loss of colour, and the necessary washing makes the shade much lighter, and, further, that in use the colour bleeds, which for many purposes renders it utterly unfit for use.

This fault of 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, and on account of the error 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, after digestion with water for three hours at 50° C., settle, leaving the water quite clear, or but very slightly tinged; dry should also be similarly tested in alcohol, glycerine, and turpentine.

The action of heat in some cases causes the shade materially to alter. 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 but by its property of combining with the acid scarlet, among some ponceaux, such as ponceau 4 RB (Berlin), and greens precipitated by arsenious acid in which great care has not been taken; and it may be taken as a general rule that a good lake can be dried at 100° C. without undergoing any change, but it is always advisable to dry them at a temperature a little over 50° C. If they change, the conclusions to be drawn are, either the colours have not been properly combined to form true pigments, a cheap class of colour is being used or one that has not been properly examined, or the pigment has been faultily made. Changes caused by heat under 100° C. are generally due to improper manipulation in some part of the process.

CHAPTER XII

WASHING, FILTERING, AND FINISHING

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 in the manufacture of the lake, for, unless they are entirely removed, it is useless to look for the fullest and brightest shades; and, further, their presence often acting on the various media used in their application renders them useless for the purposes for which the pigments were made, and it will be found that in at least fifty 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 by far the more rapid, and is extremely effective where the pigment is of an open and granular texture, *e.g.* such as imitation red lead, vermilionettes; but in colours of a more gelatinous nature, especially high-class lakes sold in the pulp form, it is by far the better plan to wash by decantation, for time is required to enable the impurities retained in particles of the lake to diffuse into the wash water. Experience has shown that when, in a case of urgency, one part of a batch of colour has been washed in a filter press it has been rejected, yet the other part washed by decantation has given every satisfaction. It, however, must be borne in mind that the purpose for which the pigment is required determines in a great measure which process of washing should be adopted. Colours for use in oil, *i.e.* pigments used by paint grinders, linoleum manufacturers, etc., can be effectively washed by the filter press; but for high-class lakes, more especially those used as pulp colours and containing a high proportion of hydrate of aluminium on 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 much more rapidly and clearly with the first water, and much more slowly with each successive washing. This is not due to any action of the water, 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 be represented by 100, the first water taken off removes 75 per cent., leaving but 25 per cent. in the tank with the lake, the second leaves but 6·25 per cent., and the third but 1·5625, fully two-thirds of which are subsequently removed by filtration and pressing.

It is advisable when the nature of the salts, etc., in solution have no action on the pigment, to allow as long as possible for the lake to settle the first time, as this water contains by far the greater quantities of salts, etc., and in cases of urgency it is better to take off one water after complete settlement than to remove two or three after partial settlement. As a general rule it is, however, advisable to remove the first water 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 lakes 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 but only partially, leaving a haze of more or less density, the practice of adding a little soda or alum to clear the liquid is strongly to be deprecated, as it in nearly every case injures the pigment, and the loss caused by running off the haze together with the last water is but very small as a general rule, and it is wiser to suffer the small 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 being made, and the extent and action of the mistake made.

Filtering the pigment after making and washing can be carried out in several ways. For dry colours, the filter press is by a long way the best method to adopt, as it can be so regulated as to give the pressed and filtered pigment in such a state that it requires but little time to thoroughly dry.

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 p. 117 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 half of the cylinder marked U or U′ is about half filled. The taps T 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. can readily be obtained. 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.

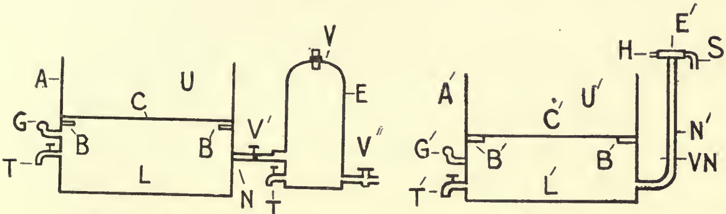


FIG I

FIG II

Figs. 1 and 2.—A and A′, ¼ in. iron C. B and B′, Flanges to support C and C′. C and C′, ¼ in. perforated iron plates. T T′ and T, Taps to run off the filtrate. V V′ V″, ½ in. valves. G and G′, Vacuum gauges. L, Condensation chamber, ¼ 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, 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 partially cool. 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 often stiffens too much at the bottom, which gives 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; for instance, tannic acid lakes, which are blackened and discoloured by contact with iron.

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, which, however, takes from a couple of days to a week to complete the operation; but, when complete, a slight finish is given in a hydraulic press. This method, though tedious for many lakes, gives a much more homogeneous paste, and 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 the case of pulp colours, and the great point to be aimed at in pulp colours is always to send any given pulp out with the same percentage of moisture; for most of these pastes are used with size, and if the lake contain too much water when it is used it seems to have no body, and appears transparent; if it is too dry, it thickens the size too much, rendering it unusable, because if more size is used than usual the shade and appearance entirely differ.

Dry colours are sold in lumps, drops, and powder. When lumps are wanted, it is customary to roughly break the dried lake. 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 simply added for the purpose of binding 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 before being sent to the machine a little gum is also used. When a lake has to be powdered, it is not advisable to press it too hard or dry it too quickly, as the friability is therefore much diminished, and it does not grind so easily. Powders must all be carefully sieved before they are despatched, otherwise particles not completely ground together with gritty matter will be found in the ground pigment, deteriorating its quality.

CHAPTER XIII

MATCHING AND TESTING LAKE PIGMENTS

The form in which the samples to be matched come to the lake-maker are many, from less than a square inch of coloured paper to a pound of the pigment required to be matched.

In cases where the only sample given is but a small piece of coloured paper, an experienced lake-maker can readily 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 in many instances, where the piece of paper has either been rolled, glazed, or varnished, to ascertain the actual shade the pigment is required to match. Where the sample supplied is a fair one, say an ounce or so, it is by far the better plan to make an assay of the colour. This can be readily carried out by dividing it into two parts, namely—

I. Examination of the colouring-matters.
II. Examination of the base.

The examination of the colouring-matter.—Take a small portion of the pigment and rub it evenly out on a piece of paper with a little size or gum to make it adhere, and dry it at about 40–50° C. When dry, carefully compare the shade with the working standards, noting what colours and "makes" most nearly approximate it. Carefully feel the surface; if it feels rough, a ground mineral base may be expected. Note the fulness, density, and brilliancy of the shade, as these properties, when considered in conjunction with the results yielded by an examination of the base, suggest often 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 at that temperature; for, as previously mentioned, if the colour be a maroon, and it changes a good deal at 100° C., it is to be inferred that the magenta is not combined save with the acid colour, and therefore a match will have to be so produced to compete with it in price; or it may, in other cases, show some weakness, which has caused the user to look for another source of supply, in order to get rid of this fault, and in consequence puts the matcher on his guard to avoid such error.

Divide the remaining piece of the paper, and spot one piece with a drop each of 10 per cent. solution, and strong nitric and hydrochloric acids, and watch the result; and, by reference to the valuable tables compiled by various authors, determine, along with indications previously obtained by comparison with lakes of known composition, the group to which the colour or colours belong, confirming the indications by further tests of 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 identifying the colour which has been used in the greatest quantity, but to determine what colours have been used to modify the shade.

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

Yellow lakes that are made are usually those of naphthol yellow S, auramine, thioflavine T, quinoline yellow, and metanil yellow, and examination of the standard shade would quickly show which colour in all probability the lake was derived from, for of the barium lakes 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 the acids would further aid the detection, for—

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

Metanil yellow—with hydrochloric acid goes much redder, and with nitric acid yields almost a scarlet.

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

Quinoline yellow—hydrochloric acid has very little action; nitric acid turns it redder.

Thioflavine T is like auramine, at once decolorised by both hydrochloric and nitric acids, but unlike auramine, when treated with caustic soda, goes reddish instead of decolorising.

The orange lakes are almost entirely derived from azo colours, and the various prices of these colours gives one an idea which one will have to be used when the price of the lake is known, and all lake-makers are sure to have several standards of almost identical shades, but of very different prices, according to the nature of the lake pigment required. The principal orange colours met with are the mandarin R and G (Ber.), orange II, brilliant orange R and G, ponceau

4GBL. Their behaviour 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 it is thrown down with, and the price limit. As often as not the lakes are mixtures of a cheap and a more expensive dyestuff, the cheaper colour being used to give the intensity and fulness, the better one to give greater brilliancy and fastness; and the colour-maker for his own purposes should keep a series of orange lakes of as great a variety of shades and cost as he can manage to make, for it is only by such means that he is able to obtain an idea as to what are the colours used to make 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; and 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 pretty 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 very readily recognised after a very little experience. The peculiar bright bloom and intensity of the colour leaves very little room for doubt, and very short exposure to light—two or three hours in bright sunshine—will soon confirm such an idea, as the colour would even then, if derived from an eosine, show signs of fading. The identification of a particular eosine is not a matter of such great ease, but nearly all eosine lakes are toned with the addition of various basic colours to give any particular 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 not very often met with.

Eosines, however, precipitated immediately, go 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 turn yellow much more slowly on the addition of acids, and do not appear to change under the influence of dilute alkalies; further, their shade and appearance prevents them being mistaken for ponceau lakes, after having dealt with the various red lakes but a short time.

The fast or permanent reds show but little change when treated with both acids and alkalies. This together with their superior fastness to all but alizarine lakes to light gives a ready means of identifying them.

Of the great number of ponceau or scarlet lakes it is advisable for a lake-pigment maker to select a limited number, say nine, whose properties and chemistry he has rendered himself thoroughly conversant with, and to use these as his scarlets for the production of all lakes derived from this source; for to use a separate colour for each individual shade causes the number and variety of dyestuffs to rapidly accumulate, 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, in various stages of adulteration, but of price and properties. It will then be found that he can, having once determined his standards, readily match at a given price any lake pigment derived from this class, by judicious admixture of the various scarlets he has at command. If a special case arises, it is a simple matter to go carefully into the colouring-matter in such a lake, and to obtain a colour with the properties desired, if he has not it already at his disposal.

Pure magenta, rhodamine, and safranine lakes are readily identified by their characteristic shades, but are far more difficult to recognise when used in mixtures with other colours. Magenta is largely used along with blue shades of ponceau to produce maroon lakes. Safranines are also used for this purpose, but to a much less extent, as their greater cost militates against their use; but boiling a little of the lake with a solution of sodium carbonate at once, by dissolving the magenta or safranine, indicates its presence, and according to the depth and colour of the lake the amount can usually then be readily gauged.

Rhodamines are used with eosine to give blue shades, and usually indicate their presence by the action they have in this respect on the shade; and on treatment with acid a lake containing eosine and rhodamine does not become so readily yellow as is the case when a pure eosine is alone used.

Violet lakes, save those derived from gallein, which go brown on treatment with acids, are for the most part derived from methyl violet, which goes blue on treatment with acids. The shade is modified by the addition of rhodamines, magenta, etc., the proportion of which, together with what colour to use, is best determined by comparison with lakes of known composition, as the complications arising from endeavouring to isolate the modifying colour in such mixtures makes it a task of considerable time and patience; and as this class of lakes are not used to any very large extent, the trouble is best met by having a series of modified violets to refer to.

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. In this case 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, 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 which particular colouring-matter was required to match a given sample.

The blues derived from allied alizarine colours are not met with in commerce to any great extent; but those from such colours as the erioglaucines and colours of similar constitution are readily recognised by their pure shade, and being extremely sensitive to the action of both acids and alkalies.

Brown lakes are an unimportant class, and are mainly derived from Bismarck brown modified with other colours, which the shade shows of what nature. 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 between the lakes produced by them is very great, and they are readily recognised as being produced from acid colours, and the shade in nearly every instance indicates to the experienced lake-maker which brand to use.

Black lakes, save for tinting purposes, are not much in demand, and usually one made from some good black colouring-matter will meet the requirements. Black lakes of a full deep colour are difficult to produce, inclining often to be more of a deep navy-blue colour. Where a full deep black is met with, it is usually either some 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 can generally be taken for granted 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 by incineration in the crucible are usually driven off or burnt, and the base or bases and the precipitating agent remains. The presence of aluminium, iron, lead, or other inorganic matters are left, and as they are soluble, for the most part, in hydrochloric acid at the boil, they can readily be detected by ordinary qualitative analysis. The insoluble residue can readily be identified, as it usually consists of either clay, barium sulphate, calcium sulphate, or mixtures of these, which with a little practice are identified without proceeding to a complete analysis. By watching the base when boiling with hydrochloric acid, the peculiar effect of the action of calcium sulphate indicates its presence. Clay does not settle so readily as barium sulphate, but an intimate mixture of clay and precipitated barium sulphate is rather difficult to casually determine; but washing and drying the residue will enable the presence of clay to be determined, as it imparts a peculiar shiny appearance to the dried residue. 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.

Sample of orange lake to be matched, gave a smooth bright lake, intermediate in shade by those produced from orange II and mandarin R (Ber.). The lake when incinerated showed the presence of aluminium and a considerable amount of barium sulphate and some clay evidently. 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 result was the shade was about right, 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 very considerably on heating, gave a base very similar to the one 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 the result induced. The trial of the addition of a brown colouring-matter, a proportion of acid brown B (Basle), was used along with the ponceau, but the shade, though nearer, was not correct; but on using a mixture of Bismarck brown and magenta the shade was finally determined.

A bright scarlet lake, which examination of the base showed to be a mixture of blanc-fixe and aluminium hydrate, was much redder than ponceau GL (Ber.), much brighter than scarlet GR, much yellower than scarlet 3R (M. L. & B.), was matched by a mixture of scarlet 3R, ponceau GL, and orange II, after a couple of trials to exactly determine the correct quantities.

INDEX

PRINTED BY MORRISON AND GIBB LIMITED, EDINBURGH

Abridged Catalogue
OF
Special Technical Books.

INDEX TO SUBJECTS.

PAGE
Adhesives 10
Agricultural Chemistry ... 9
Air, Industrial Use of ... 10
Alcohol, Industrial ... 9
Alum and its Sulphates ... 8
Ammonia 8
Aniline Colours 3
Animal Fats 6
Anti-corrosive Paints ... 4
Architecture, Terms in ... 22
Architectural Pottery ... 12
Artificial Lighting 20
Artificial Perfumes ... 7
Balsams 9
Bleaching Agents, etc. ... 17
Bone Products 8
Bookbinding 23
Brick-making ... 11, 12
Burnishing Brass 21
Carpet Yarn Printing ... 16
Casein 4
Celluloid 23
Cement 22
Ceramic Books ... 11, 12
Charcoal 8
Chemical Analysis... ... 8
Chemical Essays 8
Chemical Reagents ... 8
Chemical Works 8
Clays 12
Coal-dust Firing 19
Colliery Recovery Work... 18
Colour Matching (Textile) 16
Colour-mixing for Dyers... 16
Colour Recipes 3
Colour Theory 16
Combing Machines ... 18
Compounding Oils, etc. ... 6
Condensing Apparatus ... 19
Cosmetics 7
Cotton Dyeing 17
Cotton Spinning 17
Cotton Waste 18
Cranes and Hoists ... 20
Damask Weaving 15
Dampness in Buildings ... 22
Decorators' Books ... 4
Decorative Textiles ... 15
Dental Metallurgy... ... 18
Disinfection 9
Driers 5
Drugs 22
Drying Oils 5
Drying with Air, etc. ... 10
Dyeing Marble 23
Dyeing Woollen Fabrics... 17
Dyers' Materials 16
Dye-stuffs 17
Edible Fats and Oils ... 7
Electric Lamp Development 21
Electric Wiring 21
Electricity in Collieries ... 18
Emery 24
Enamelling Metal 13
Enamels 13
Engineering Handbooks ... 19

PAGE
Engraving 23
Essential Oils 7
Evaporating Apparatus ... 19
External Plumbing ... 20
Fats 6, 7
Faults in Woollen Goods 15
Flax Spinning 18
Food and Drugs 22
Foundry Machinery ... 20
Fruit Preserving 23
Gas and Oil Engines ... 19
Gas Firing 19
Glass-making Recipes ... 13
Glass Painting 13
Glue-making and Testing... 8
Greases 6
Gutta Percha 11
Hat Manufacturing ... 15
Hemp Spinning 18
History of Staffs Potteries 12
Hops 21
Hot-water Supply ... 21
India-rubber... 11
India-rubber Substitutes 5
Inks 3, 4, 5, 9
Insecticides, etc. 21
Iron-corrosion 4
Iron, Science of 19
Iron and Steel Work ... 19
Japanning 21
Jute Spinning 18
Lace-Making 15
Lacquering 21
Lake Pigments 3
Lead 10
Leather-working Mater'ls 6, 11
Libraries 24
Linoleum 5
Lithographic Inks 5
Lithography 23
Lubricants 6
Manures 8, 9
Meat Preserving 23
Medicated Soaps 7
Metal Polishing Soaps ... 7
Mineral Pigments 3
Mineral Waxes 6
Mine Ventilation 18
Mine Haulage 18
Mining, Electricity ... 18
Motor Car Mechanism ... 20
Needlework 15
Oil and Colour Recipes ... 3
Oil Boiling 5
Oilmen's Sundries ... 3
Oil Merchants' Manual ... 6
Oils 5, 6, 7
Ozone, Industrial Use of... 10
Paint Manufacture ... 3
Paint Materials 3
Paint-material Testing ... 4
Paint Mixing ... 3, 4
Paper-Mill Chemistry ... 13
Paper-pulp Dyeing ... 13
Petroleum 6
Pigments 3, 9
Plumbers' Books ... 20, 21

PAGE
Pottery Clays 21
Pottery Decorating ... 11
Pottery Manufacture 11, 12
Pottery Marks 12
Power-loom Weaving ... 14
Preserved Foods 23
Printers' Ready Reckoner 23
Printing Inks ... 3, 4, 5
Recipes 3, 13
Reinforced Concrete ... 19
Resins 9
Ring Spinning Frame ... 18
Risks of Occupations ... 10
Riveting China, etc. ... 12
Scheele's Essays 8
Sealing Waxes 10
Shale Oils and Tars ... 9
Shoe Polishes 6
Silk Dyeing 17
Silk Throwing, etc. ... 17
Smoke Prevention... ... 19
Soap Powders 7
Soaps... 7
Spinning 15, 17, 18
Spirit Varnishes 5
Staining Marble, and Bone 23
Stain-removing Soaps ... 7
Steam Drying 10
Steam Turbines 20
Steel Hardening 19
Sugar Technology ... 24
Sweetmeats... 23
Tallow 6
Technical Schools, List ... 24
Terra-cotta 11
Testing Paint Materials ... 4
Textile Design 15
Textile Fabrics ... 14, 15
Textile Fibres 14
Textile Materials 14
Timber 22
Toilet Soapmaking ... 7
Toothed Gearing 19
Varnishes 5
Vegetable Fats and Oils ... 7
Vegetable Preserving ... 23
Warp Sizing 16
Waste Utilisation 9
Water, Industrial Use ... 10
Water-proofing Fabrics ... 16
Waxes 6
Weaving Calculations ... 15
White Lead and Zinc ... 5
Wiring Calculations ... 21
Wood Distillation ... 22
Wood Extracts 22
Wood Waste Utilisation... 22
Wood-Dyeing 23
Wool-Dyeing 17
Woollen Goods ... 15, 16, 17
Woven Fabrics 16
Writing Inks 9
X-Ray Work 11
Yarn Sizing 16
Yarn Numbering and Testing 14, 15
Zinc White Paints ... 5

PUBLISHED BY
SCOTT, GREENWOOD & SON,
8 BROADWAY, LUDGATE, LONDON, E.C.

FULL PARTICULARS OF CONTENTS

Of the Books mentioned in this **ABRIDGED CATALOGUE** will be found in the following Catalogues of

CURRENT TECHNICAL BOOKS.

LIST I.

Artists' Colours—Bone Products—Butter and Margarine Manufacture—Casein—Cements—Chemical Works (Designing and Erection)—Chemistry (Agricultural, Industrial, Practical and Theoretical)—Colour Mixing—Colour Manufacture—Compounding Oils—Decorating—Driers—Drying Oils—Drysaltery—Emery—Essential Oils — Fats (Animal, Vegetable, Edible) — Gelatines — Glues — Greases — Gums — Inks — Lead—Leather — Lubricants — Oils — Oil Crushing — Paints — Paint Manufacturing — Paint Material Testing—Perfumes—Petroleum—Pharmacy—Recipes (Paint, Oil and Colour — Resins—Sealing Waxes—Shoe Polishes — Soap Manufacture — Solvents — Spirit Varnishes—Varnishes—White Lead—Workshop Wrinkles.

LIST II.

Bleaching — Bookbinding — Carpet Yarn Printing — Colour (Matching, Mixing Theory)—Cotton Combing Machines—Dyeing (Cotton, Woollen and Silk Goods) — Dyers' Materials—Dye-stuffs—Engraving—Flax, Hemp and Jute Spinning and Twisting —Gutta-Percha — Hat Manufacturing — India-rubber — Inks — Lace-making — Lithography—Needlework—Paper Making — Paper-Mill Chemist — Paper-pulp Dyeing — Point Lace—Power-loom Weaving—Printing Inks—Silk Throwing—Smoke Prevention—Soaps—Spinning—Textile (Spinning, Designing, Dyeing, Weaving, Finishing —Textile Materials—Textile Fabrics—Textile Fibres—Textile Oils—Textile Soaps—Timber—Water (Industrial Uses)—Water-proofing—Weaving—Writing Inks—Yarns Testing, Sizing).

LIST III.

Architectural Terms—Brassware (Bronzing, Burnishing, Dipping, Lacquering)—Brickmaking—Building—Cement Work—Ceramic Industries—China—Coal-dust Firing —Colliery Books—Concrete—Condensing Apparatus—Dental Metallurgy—Drainage—Drugs—Dyeing—Earthenware—Electrical Books—Enamelling—Enamels—Engineering Handbooks—Evaporating Apparatus—Flint Glass-making—Foods—Food Preserving—Fruit Preserving—Gas Engines—Gas Firing — Gearing — Glassware (Painting, Riveting)—Hops—Iron (Construction, Science)—Japanning—Lead—Meat Preserving —Mines (Haulage, Electrical Equipment, Ventilation, Recovery Work from)—Plants (Diseases, Fungicides, Insecticides)—Plumbing Books—Pottery (Architectural, Clays, Decorating, Manufacture, Marks on) — Reinforced Concrete — Riveting (China, Earthenware, Glassware)—Sanitary Engineering—Steam Turbines—Steel (Hardening, Tempering)—Sugar—Sweetmeats—Toothed Gearing—Vegetable Preserving — Wood Dyeing—X-Ray Work.

COPIES OF ANY OF THESE LISTS WILL BE SENT POST FREE ON APPLICATION.

(Paints, Colours, Pigments and Printing Inks.)

THE CHEMISTRY OF PIGMENTS. By ERNEST J. PARRY, B.Sc. (Lond.), F.I.C., F.C.S., and J. H. COSTE, F.I.C., F.C.S. Demy 8vo. Five Illustrations. 285 pp. Price 10s. 6d. net. (Post free, 10s. 10d. home; 11s. 3d. abroad.)

THE MANUFACTURE OF PAINT. A Practical Handbook for Paint Manufacturers, Merchants and Painters. By J. CRUICKSHANK SMITH, B.Sc. Demy 8vo.

[*New Edition in Preparation.*

DICTIONARY OF CHEMICALS AND RAW PRODUCTS USED IN THE MANUFACTURE OF PAINTS, COLOURS, VARNISHES AND ALLIED PREPARATIONS. By GEORGE H. HURST, F.C.S. Demy 8vo. 380 pp. Price 7s. 6d. net. (Post free, 8s. home; 8s. 6d. abroad.)

THE MANUFACTURE OF LAKE PIGMENTS FROM ARTIFICIAL COLOURS. By FRANCIS H. JENNISON, F.I.C., F.C.S. **Sixteen Coloured Plates, showing Specimens of Eighty-nine Colours, specially prepared from the Recipes given in the Book.** 136 pp. Demy 8vo. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. abroad.)

THE MANUFACTURE OF MINERAL AND LAKE PIGMENTS. Containing Directions for the Manufacture of all Artificial, Artists and Painters' Colours, Enamel, Soot and Metallic Pigments. A text-book for Manufacturers, Merchants, Artists and Painters. By Dr. JOSEF BERSCH. Translated by A. C. WRIGHT, M.A. (Oxon.), B.Sc. (Lond.). Forty-three Illustrations. 476 pp. Demy 8vo. Price 12s. 6d. net. (Post free, 13s. home; 13s. 6d. abroad.)

RECIPES FOR THE COLOUR, PAINT, VARNISH, OIL, SOAP AND DRYSALTERY TRADES. Compiled by AN ANALYTICAL CHEMIST. 330 pp. Second Revised and Enlarged Edition. Demy 8vo. Price 10s. 6d. net. (Post free, 11s. home; 11s. 3d. abroad.)

OILMEN'S SUNDRIES AND HOW TO MAKE THEM. Being a Collection of Practical Recipes for Boot Polishes, Blues, Metal Polishes, Disinfectants, etc., compiled from "Oils, Colours and Drysalteries". Crown 8vo. 130 pages. Price 2s. 6d. net. (Post free, 2s. 9d. home; 2s. 10d. abroad.)

OIL COLOURS AND PRINTERS' INKS. By LOUIS EDGAR ANDÉS. Translated from the German. 215 pp. Crown 8vo. 56 Illustrations. Price 5s. net. (Post free, 5s. 4d. home; 5s. 6d. abroad.)

MODERN PRINTING INKS. A Practical Handbook for Printing Ink Manufacturers and Printers. By ALFRED SEYMOUR. Demy 8vo. Six Illustrations. 90 pages. Price 5s. net. (Post free, 5s. 4d. home; 5s. 6d. abroad.)

THREE HUNDRED SHADES AND HOW TO MIX THEM. For Architects, Painters and Decorators. By A. DESAINT, Artistic Interior Decorator of Paris. The book contains 100 folio Plates, measuring 12 in. by 7 in., each Plate containing specimens of three artistic shades. These shades are all numbered, and their composition and particulars for mixing are fully given at the beginning of the book. Each Plate is interleaved with grease-proof paper, and the volume is very artistically bound in art and linen with the Shield of the Painters' Guild impressed on the cover in gold and silver. Price 21s. net. (Post free, 21s. 6d. home; 22s. 6d. abroad.)

HOUSE DECORATING AND PAINTING. By W. NORMAN BROWN. Eighty-eight Illustrations. 150 pp. Crown 8vo. Price 3s. 6d. net. (Post free, 3s. 9d. home and abroad.)

A HISTORY OF DECORATIVE ART. By W. NORMAN BROWN. Thirty-nine Illustrations. 96 pp. Crown 8vo. Price 1s. net. (Post free, 1s. 3d. home and abroad.)

WORKSHOP WRINKLES for Decorators, Painters, Paperhangers, and Others. By W. N. BROWN. Crown 8vo. 128 pp. Second Edition. Price 2s. 6d. net. (Post free, 2s. 9d. home; 2s. 10d. abroad.)

CASEIN. By ROBERT SCHERER. Translated from the German by CHAS. SALTER. Demy 8vo. Illustrated. Second Revised English Edition. 160 pp. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. abroad.)

SIMPLE METHODS FOR TESTING PAINTERS' MATERIALS. By A. C. WRIGHT, M.A. (Oxon.), B.Sc. (Lond.). Crown 8vo. 160 pp. Price 5s. net. (Post free, 5s. 3d. home; 5s. 6d. abroad.)

IRON-CORROSION, ANTI-FOULING AND ANTI-CORROSIVE PAINTS. Translated from the German of LOUIS EDGAR ANDÉS. Sixty-two Illustrations. 275 pp. Demy 8vo. Price 10s. 6d. net. (Post free, 10s. 10d. home; 11s. 3d. abroad.)

THE TESTING AND VALUATION OF RAW MATERIALS USED IN PAINT AND COLOUR MANUFACTURE. By M. W. JONES, F.C.S. A Book for the Laboratories of Colour Works. 88 pp. Crown 8vo. Price 5s. net. (Post free, 5s. 3d. home and abroad.)

For contents of these books, see List I.

THE MANUFACTURE AND COMPARATIVE MERITS OF WHITE LEAD AND ZINC WHITE PAINTS. By G. Petit, Civil Engineer, etc. Translated from the French. Crown 8vo. 100 pp. Price 4s. net. (Post free, 4s. 3d. home; 4s. 4d. abroad.)

STUDENTS' HANDBOOK OF PAINTS, COLOURS, OILS AND VARNISHES. By John Furnell. Crown 8vo. 12 Illustrations. 96 pp. Price 2s. 6d. net. (Post free, 2s. 9d. home and abroad.)

PREPARATION AND USES OF WHITE ZINC PAINTS. Translated from the French of P. Fleury. Crown 8vo. 280 pages. Price 6s. net. (Post free, 6s. 4d. home; 6s. 6d. abroad.)

(Varnishes and Drying Oils.)

THE MANUFACTURE OF VARNISHES AND KINDRED INDUSTRIES. By J. Geddes McIntosh. Second, greatly enlarged, English Edition, in three Volumes, based on and including the work of Ach. Livache.

Volume I.—**OIL CRUSHING, REFINING AND BOILING, THE MANUFACTURE OF LINOLEUM, PRINTING AND LITHOGRAPHIC INKS, AND INDIA-RUBBER SUBSTITUTES.** Demy 8vo. 150 pp. 29 Illustrations. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. abroad.)

Volume II.—**VARNISH MATERIALS AND OIL-VARNISH MAKING.** Demy 8vo. 70 Illustrations. 220 pp. Price 10s. 6d. net. (Post free, 10s. 10d. home; 11s. 3d. abroad.)

Volume III.—**SPIRIT VARNISHES AND SPIRIT VARNISH MATERIALS.** Demy 8vo. Illustrated. 464 pp. Price 12s. 6d. net. (Post free, 13s. home; 13s. 6d. abroad.)

DRYING OILS, BOILED OIL AND SOLID AND LIQUID DRIERS. By L. E. Andés. Expressly Written for this Series of Special Technical Books, and the Publishers hold the Copyright for English and Foreign Editions. Forty-two Illustrations. 342 pp. Demy 8vo. Price 12s. 6d. net. (Post free, 13s. home; 13s. 3d. abroad.)

(*Analysis of Resins, see page* 9.)

(Oils, Fats, Waxes, Greases, Petroleum.)

LUBRICATING OILS, FATS AND GREASES: Their Origin, Preparation, Properties, Uses and Analyses. A Handbook for Oil Manufacturers, Refiners and Merchants, and the Oil and Fat Industry in General. By GEORGE H. HURST, F.C.S. Third Revised and Enlarged Edition. Seventy-four Illustrations. 384 pp. Demy 8vo. Price 10s. 6d. net. (Post free, 11s. home; 11s. 3d. abroad.)

TECHNOLOGY OF PETROLEUM: Oil Fields of the World—Their History, Geography and Geology—Annual Production and Development—Oil-well Drilling—Transport. By HENRY NEUBERGER and HENRY NOALHAT. Translated from the French by J. G. MCINTOSH. 550 pp. 153 Illustrations. 26 Plates. Super Royal 8vo. Price 21s. net. (Post free, 21s. 9d. home; 23s. 6d. abroad.)

MINERAL WAXES: Their Preparation and Uses. By RUDOLF GREGORIUS. Translated from the German. Crown 8vo. 250 pp. 32 Illustrations. Price 6s. net. (Post free, 6s. 4d. home; 6s. 6d. abroad.)

THE PRACTICAL COMPOUNDING OF OILS, TALLOW AND GREASE FOR LUBRICATION, ETC. By AN EXPERT OIL REFINER. Second Edition. 100 pp. Demy 8vo. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. abroad.)

THE MANUFACTURE OF LUBRICANTS, SHOE POLISHES AND LEATHER DRESSINGS. By RICHARD BRUNNER. Translated from the Sixth German Edition by CHAS. SALTER. 10 Illustrations. Crown 8vo. 170 pp. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. abroad.)

THE OIL MERCHANTS' MANUAL AND OIL TRADE READY RECKONER. Compiled by FRANK F. SHERRIFF. Second Edition Revised and Enlarged. Demy 8vo. 214 pp. With Two Sheets of Tables. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. 3d. abroad.)

ANIMAL FATS AND OILS: Their Practical Production, Purification and Uses for a great Variety of Purposes. Their Properties, Falsification and Examination. Translated from the German of LOUIS EDGAR ANDÉS. Sixty-two Illustrations. 240 pp. Second Edition, Revised and Enlarged. Demy 8vo. Price 10s. 6d. net. (Post free, 10s. 10d. home; 11s. 3d. abroad.)

For contents of these books, see List I.

VEGETABLE FATS AND OILS: Their Practical Preparation, Purification and Employment for Various Purposes, their Properties, Adulteration and Examination. Translated from the German of Louis Edgar Andés. Ninety-four Illustrations. 340 pp. Second Edition. Demy 8vo. Price 10s. 6d. net. (Post free, 11s. home; 11s. 6d. abroad.)

EDIBLE FATS AND OILS: Their Composition, Manufacture and Analysis. By W. H. Simmons, B.Sc. (Lond.), and C. A. Mitchell, B.A. (Oxon.). Demy 8vo. 150 pp. Price 7s. 6d. net. (Post free, 7s. 9d. home; 8s. abroad.)

(Essential Oils and Perfumes.)

THE CHEMISTRY OF ESSENTIAL OILS AND ARTIFICIAL PERFUMES. By Ernest J. Parry, B.Sc. (Lond.), F.I.C., F.C.S. Second Edition, Revised and Enlarged. 552 pp. 20 Illustrations. Demy 8vo. Price 12s. 6d. net. (Post free, 13s. home; 13s. 6d. abroad.)

(Soap Manufacture.)

SOAPS. A Practical Manual of the Manufacture of Domestic, Toilet and other Soaps. By George H. Hurst, F.C.S. 2nd edition. 390 pp. 66 Illustrations. Demy 8vo. Price 12s. 6d. net. (Post free, 13s. home; 13s. 6d. abroad.)

TEXTILE SOAPS AND OILS. Handbook on the Preparation, Properties and Analysis of the Soaps and Oils used in Textile Manufacturing, Dyeing and Printing. By George H. Hurst, F.C.S. Crown 8vo. 195 pp. Price 5s. net. (Post free, 5s. 4d. home; 5s. 6d. abroad.)

THE HANDBOOK OF SOAP MANUFACTURE. By Wm. H. Simmons, B.Sc. (Lond.), F.C.S. and H. A. Appleton. Demy 8vo. 160 pp. 27 Illustrations. Price 8s. 6d. net. (Post free, 8s. 10d. home; 9s. abroad.)

MANUAL OF TOILET SOAPMAKING, including Medicated Soaps, Stain-removing Soaps, Metal Polishing Soaps, Soap Powders and Detergents. Translated from the German of Dr. C. Deite. Demy quarto. 150 pages. 79 Illustrations. Price 12s. 6d. net. (Post free, 13s. home; 13s. 6d. abroad.)

(Cosmetical Preparations.)

COSMETICS: MANUFACTURE, EMPLOYMENT AND TESTING OF ALL COSMETIC MATERIALS AND COSMETIC SPECIALITIES. Translated from the German of Dr. Theodor Koller. Crown 8vo. 262 pp. Price 5s. net. (Post free, 5s. 4d. home; 5s. 6d. abroad.)

(Glue, Bone Products and Manures.)

GLUE AND GLUE TESTING. By Samuel Rideal, D.Sc. (Lond.), F.I.C. Fourteen Engravings. 144 pp. Demy 8vo. Price 10s. 6d. net. (Post free, 10s. 10d. home; 11s. abroad.)

BONE PRODUCTS AND MANURES: An Account of the most recent Improvements in the Manufacture of Fat, Glue, Animal Charcoal, Size, Gelatine and Manures. By Thomas Lambert, Technical and Consulting Chemist. Second Revised Edition. Demy 8vo. 172 pages. 17 Illustrations. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. abroad.)

(*See also Chemical Manures, p.* 9.)

(Chemicals, Waste Products, etc.)

REISSUE OF **CHEMICAL ESSAYS OF C. W. SCHEELE.** First Published in English in 1786. Translated from the Academy of Sciences at Stockholm, with Additions. 300 pp. Demy 8vo. Price 5s. net. (Post free, 5s. 6d. home; 5s. 9d. abroad.)

THE MANUFACTURE OF ALUM AND THE SULPHATES AND OTHER SALTS OF ALUMINA AND IRON. Their Uses and Applications as Mordants in Dyeing and Calico Printing, and their other Applications in the Arts Manufactures, Sanitary Engineering, Agriculture and Horticulture. Translated from the French of Lucien Geschwind. 195 Illustrations. 400 pp. Royal 8vo. Price 12s. 6d. net. (Post free, 13s. home; 13s. 6d. abroad.)

AMMONIA AND ITS COMPOUNDS: Their Manufacture and Uses. By Camille Vincent, Professor at the Central School of Arts and Manufactures, Paris. Translated from the French by M. J. Salter. Royal 8vo. 114 pp. Thirty-two Illustrations. Price 5s. net. (Post free, 5s. 4d. home; 5s. 6d. abroad.)

CHEMICAL WORKS: Their Design, Erection, and Equipment. By S. S. Dyson and S. S. Clarkson. Royal 8vo. 220 pp. With 9 Folding Plates and 80 Illustrations. Price 21s. net. (Post free, 21s. 6d. home; 22s. abroad.)

MANUAL OF CHEMICAL ANALYSIS, as applied to the Assay of Fuels, Ores, Metals, Alloys, Salts and other Mineral Products. By E. Prost, D.Sc. Translated by J. Cruickshank Smith, B.Sc. Royal 8vo. 300 pages. 44 Illustrations. Price 12s. 6d. net. (Post free, 13s. home; 13s. 6d. abroad.)

TESTING OF CHEMICAL REAGENTS FOR PURITY. Translated from the German of Dr. C Krauch. Royal 8vo. 350 pages. Price 12s. 6d. net. (Post free 13s. home; 13s. 6d. abroad.)

For contents of these books, see List I.

SHALE OILS AND TARS and their Products. By Dr. W. Scheithauer. Translated from the German. Demy 8vo. 190 pages. 70 Illustrations and 4 Diagrams. Price 8s. 6d. net. (Post free, 8s. 10d. home; 9s. abroad). [*Just published.*

INDUSTRIAL ALCOHOL. A Practical Manual on the Production and Use of Alcohol for Industrial Purposes and for Use as a Heating Agent, as an Illuminant and as a Source of Motive Power. By J. G. McIntosh, Lecturer on Manufacture and Applications of Industrial Alcohol at The Polytechnic, Regent Street, London. Demy 8vo. 1907. 250 pp. With 75 Illustrations and 25 Tables. Price 7s. 6d. net. (Post free, 7s. 9d. home; 8s. abroad.)

THE UTILISATION OF WASTE PRODUCTS. A Treatise on the Rational Utilisation, Recovery and Treatment of Waste Products of all kinds. By Dr. Theodor Köller. Translated from the Second Revised German Edition. Twenty-two Illustrations. Demy 8vo. 280 pp. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. 3d. abroad.)

ANALYSIS OF RESINS AND BALSAMS. Translated from the German of Dr. Karl Dieterich. Demy 8vo. 340 pp. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. 3d. abroad.)

DISTILLATION OF RESINS, RESINATE LAKES AND PIGMENTS, CARBON PIGMENTS AND PIGMENTS FOR TYPEWRITING MACHINES, MANIFOLDERS, ETC. By Victor Schweizer. Demy 8vo. 185 pages. 68 Illustrations. Price 7s. 6d. net. (Post free, 8s. home; 8s. 3d. abroad.)

DISINFECTION AND DISINFECTANTS. By M. Christian. Translated from the German. Crown 8vo. 112 pages. 18 Illustrations. Price 5s. net. (Post free, 5s. 3d. home; 5s. 6d. abroad.) [*Just published.*

(Agricultural Chemistry and Manures.)

MANUAL OF AGRICULTURAL CHEMISTRY. By Herbert Ingle, F.I.C., Late Lecturer on Agricultural Chemistry, the Leeds University; Lecturer in the Victoria University. Third and Revised Edition. 400 pp. 16 Illustrations. Demy 8vo. Price 7s. 6d. net. (Post free, 8s. home; 8s. 6d. abroad.)

CHEMICAL MANURES. Translated from the French of J. Fritsch. Demy 8vo. Illustrated. 340 pp. Price 10s. 6d. net. (Post free, 11s. home; 11s. 6d. abroad.)

(*See also Bone Products and Manures, p.* 8.)

(Writing Inks and Sealing Waxes.)

INK MANUFACTURE: Including Writing, Copying, Lithographic, Marking, Stamping, and Laundry Inks. By Sigmund Lehner. Three Illustrations. Crown 8vo. 162 pp. Translated from the German of the Fifth Edition. Price 5s. net. (Post free, 5s. 3d. home; 5s. 6d. abroad.)

SEALING - WAXES, WAFERS AND OTHER ADHESIVES FOR THE HOUSEHOLD, OFFICE, WORKSHOP AND FACTORY. By H. C. STANDAGE. Crown 8vo. 96 pp. Price 5s. net. (Post free, 5s. 3d. home; 5s. 4d. abroad.)

(Lead Ores and Lead Compounds.)

LEAD AND ITS COMPOUNDS. By THOS. LAMBERT, Technical and Consulting Chemist. Demy 8vo. 226 pp. Forty Illustrations. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. 3d. abroad.)

NOTES ON LEAD ORES: Their Distribution and Properties. By JAS. FAIRIE, F.G.S. Crown 8vo. 64 pages. Price 1s. net. (Post free, 1s. 3d. home; 1s. 4d. abroad.)

(*White Lead and Zinc White Paints, see p.* 5.)

(Industrial Hygiene.)

THE RISKS AND DANGERS TO HEALTH OF VARIOUS OCCUPATIONS AND THEIR PREVENTION. By LEONARD A. PARRY, M.D., B.Sc. (Lond.). 196 pp. Demy 8vo. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. abroad.)

(Industrial Uses of Air, Steam and Water.)

DRYING BY MEANS OF AIR AND STEAM. Explanations, Formulæ, and Tables for Use in Practice. Translated from the German of E. HAUSBRAND. Second Revised English Edition. Two folding Diagrams, Thirteen Tables, and Two Illustrations. Crown 8vo. 76 pp. Price 5s. net. (Post free, 5s. 3d. home; 5s. 6d. abroad.)

(*See also* "*Evaporating, Condensing and Cooling Apparatus,*" *p.* 19.)

PURE AIR, OZONE AND WATER. A Practical Treatise of their Utilisation and Value in Oil, Grease, Soap, Paint, Glue and other Industries. By W. B. COWELL. Twelve Illustrations. Crown 8vo. 85 pp. Price 5s. net. (Post free, 5s. 3d. home; 5s. 6d. abroad.)

THE INDUSTRIAL USES OF WATER. COMPOSITION—EFFECTS—TROUBLES—REMEDIES—RESIDUARY WATERS—PURIFICATION—ANALYSIS. By H. DE LA COUX. Royal 8vo. Translated from the French and Revised by ARTHUR MORRIS. 364 pp. 135 Illustrations. Price 10s. 6d. net. (Post free, 11s. home; 11s. 6d. abroad.)

(*See Books on Smoke Prevention, Engineering and Metallurgy, p.* 19, *etc.*)

For contents of these books, see List III.

(X-Rays.)

PRACTICAL X RAY WORK. By Frank T. Addyman, B.Sc. (Lond.), F.I.C., Member of the Roentgen Society of London; Radiographer to St. George's Hospital; Demonstrator of Physics and Chemistry, and Teacher of Radiography in St. George's Hospital Medical School. Demy 8vo. Twelve Plates from Photographs of X Ray Work. Fifty-two Illustrations. 200 pp. Price 10s. 6d. net. (Post free, 10s. 10d. home; 11s. 3d. abroad.)

(India-Rubber and Gutta Percha.)

INDIA-RUBBER AND GUTTA PERCHA. Second English Edition, Revised and Enlarged. Based on the French work of T. Seeligmann, G. Lamy Torrilhon and H. Falconnet by John Geddes McIntosh. Royal 8vo. 100 Illustrations. 400 pages. Price 12s. 6d. net. (Post free, 13s. home; 13s. 6d. abroad.)

(Leather Trades.)

THE LEATHER WORKER'S MANUAL. Being a Compendium of Practical Recipes and Working Formulæ for Curriers, Bootmakers, Leather Dressers, Blacking Manufacturers, Saddlers, Fancy Leather Workers. By H. C. Standage. Demy 8vo. 165 pp. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. abroad.)

(*See also Manufacture of Shoe Polishes, Leather Dressings, etc., p.* 6.)

(Pottery, Bricks, Tiles, Glass, etc.)

MODERN BRICKMAKING. By Alfred B. Searle, Royal 8vo. 440 pages. 260 Illustrations. Price 12s. 6d. net. (Post free, 13s. home; 13s. 6d. abroad.)

THE MANUAL OF PRACTICAL POTTING. Compiled by Experts, and Edited by Chas. F. Binns. Fourth Edition, Revised and Enlarged. 200 pp. Demy 8vo. Price 17s. 6d. net. (Post free, 17s. 10d. home; 18s. 3d. abroad.)

POTTERY DECORATING. A Description of all the Processes for Decorating Pottery and Porcelain. By R. Hainbach. Translated from the German. Crown 8vo. 250 pp. Twenty-two Illustrations. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. abroad.)

A TREATISE ON CERAMIC INDUSTRIES. A Complete Manual for Pottery, Tile, and Brick Manufacturers. By Emile Bourry. A Revised Translation from the French, with some Critical Notes by Alfred B. Searle. Demy 8vo. 308 Illustrations. 460 pp. Price 12s. 6d. net. (Post free, 13s. home; 13s. 6d. abroad.)

ARCHITECTURAL POTTERY. Bricks, Tiles, Pipes, Enamelled Terra-cottas, Ordinary and Incrusted Quarries, Stoneware Mosaics, Faïences and Architectural Stoneware. By LEON LEFÊVRE. Translated from the French by K. H. BIRD, M.A., and W. MOORE BINNS. With Five Plates. 950 Illustrations in the Text, and numerous estimates. 500 pp. Royal 8vo. Price 15s. net. (Post free, 15s. 6d. home; 16s. 6d. abroad.)

CERAMIC TECHNOLOGY: Being some Aspects of Technical Science as Applied to Pottery Manufacture. Edited by CHARLES F. BINNS. 100 pp. Demy 8vo. Price 12s. 6d. net. (Post free, 12s. 10d. home; 13s. abroad.)

THE ART OF RIVETING GLASS, CHINA AND EARTHENWARE. By J. HOWORTH. Second Edition. Paper Cover. Price 1s. net. (By post, home or abroad, 1s. 1d.)

CLAY ANALYSIS AND CLAY TESTING. By A. B. SEARLE. *[In preparation.*

NOTES ON POTTERY CLAYS. The Distribution, Properties, Uses and Analyses of Ball Clays, China Clays and China Stone. By JAS. FAIRIE, F.G.S. 132 pp. Crown 8vo. Price 3s. 6d. net. (Post free, 3s. 9d. home; 3s. 10d. abroad.)

HOW TO ANALYSE CLAY. By H. M. ASHBY. Demy 8vo. 72 pp. 20 Illustrations. Price 3s. 6d. net. (Post free, 3s. 9d. home; 3s. 10d. abroad.)

A Reissue of

THE HISTORY OF THE STAFFORDSHIRE POTTERIES; AND THE RISE AND PROGRESS OF THE MANUFACTURE OF POTTERY AND PORCELAIN. With References to Genuine Specimens, and Notices of Eminent Potters. By SIMEON SHAW. (Originally published in 1829.) 265 pp. Demy 8vo. Price 5s. net. (Post free, 5s. 4d. home; 5s. 9d. abroad.)

A Reissue of

THE CHEMISTRY OF THE SEVERAL NATURAL AND ARTIFICIAL HETEROGENEOUS COMPOUNDS USED IN MANUFACTURING PORCELAIN, GLASS AND POTTERY. By SIMEON SHAW. (Originally published in 1837.) 750 pp. Royal 8vo. Price 10s. net. (Post free, 10s. 6d. home; 12s. abroad.)

BRITISH POTTERY MARKS. By G. WOOLLISCROFT RHEAD. Demy 8vo. 310 pp. With over Twelve-hundred Illustrations of Marks. Price 7s. 6d. net. (Post free, 8s. home; 8s. 3d. abroad.)

For contents of these books, see List III.

(Glassware, Glass Staining and Painting.)

RECIPES FOR FLINT GLASS MAKING. By a British Glass Master and Mixer. Sixty Recipes. Being Leaves from the Mixing Book of several experts in the Flint Glass Trade, containing up-to-date recipes and valuable information as to Crystal, Demi-crystal and Coloured Glass in its many varieties. It contains the recipes for cheap metal suited to pressing, blowing, etc., as well as the most costly crystal and ruby. Second Edition. Crown 8vo. Price 10s. 6d. net. (Post free, 10s. 9d. home; 10s. 10d. abroad.)

A TREATISE ON THE ART OF GLASS PAINTING. Prefaced with a Review of Ancient Glass. By Ernest R. Suffling. With One Coloured Plate and Thirty-seven Illustrations. Demy 8vo. 140 pp. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. abroad.)

(Paper Making, Paper Dyeing, and Testing.)

THE DYEING OF PAPER PULP. A Practical Treatise for the use of Papermakers, Paperstainers, Students and others. By Julius Erfurt, Manager of a Paper Mill. Translated into English and Edited with Additions by Julius Hübner, F.C.S., Lecturer on Papermaking at the Manchester Municipal Technical School. With illustrations and **157 patterns of paper dyed in the pulp**. Royal 8vo, 180 pp. Price 15s. net. (Post free, 15s. 6d. home; 16s. 6d. abroad).

THE PAPER MILL CHEMIST. By Henry P. Stevens, M.A., Ph.D., F.I.C. Royal 12mo. 60 illustrations. 300 pp. Price 7s. 6d. net. (Post free, 7s. 9d. home; 7s. 10d. abroad.)

THE TREATMENT OF PAPER FOR SPECIAL PURPOSES. By L. E. Andés. Translated from the German. Crown 8vo. 48 Illustrations. 250 pp. Price 6s. net. (Post free, 6s. 4d. home; 6s. 6d. abroad.)

(Enamelling on Metal.)

ENAMELS AND ENAMELLING. For Enamel Makers, Workers in Gold and Silver, and Manufacturers of Objects of Art. By Paul Randau. Second and Revised Edition. Translated from the German. With 16 Illustrations. Demy 8vo. 200 pp. Price 10s. 6d. net. (Post free, 10s. 10d. home; 11s. abroad.)

THE ART OF ENAMELLING ON METAL. By W. Norman Brown. Second Edition, Revised. Crown 8vo. 60 pp. Price 3s. 6d. net. (Post free, 3s. 9d. home; 3s. 10d. abroad.) [*Just published.*

(Textile and Dyeing Subjects.)

THE FINISHING OF TEXTILE FABRICS (Woollen, Worsted, Union and other Cloths). By Roberts Beaumont, M.Sc., M.I.Mech.E., Professor of Textile Industries, the University of Leeds; Author of "Colour in Woven Design"; "Woollen and Worsted Cloth Manufacture"; "Woven Fabrics at the World's Fair"; Vice-President of the Jury of Award at the Paris Exhibition, 1900; Inspector of Textile Institutes; Society of Arts Silver Medallist; Honorary Medallist of the City and Guilds of London Institute. With 150 Illustrations of Fibres, Yarns and Fabrics, also Sectional and other Drawings of Finishing Machinery. Demy 8vo. 260 pp. Price 10s. 6d. net. (Post free, 10s. 10d. home; 11s. 3d. abroad.)

FIBRES USED IN TEXTILE AND ALLIED INDUSTRIES. By C. Ainsworth Mitchell, B.A. (Oxon.), F.I.C., and R. M. Prideaux, F.I.C. With 66 Illustrations specially drawn direct from the Fibres. Demy 8vo. 200 pp. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. abroad.)

DRESSINGS AND FINISHINGS FOR TEXTILE FABRICS AND THEIR APPLICATION. Description of all the Materials used in Dressing Textiles: Their Special Properties, the preparation of Dressings and their employment in Finishing Linen, Cotton, Woollen and Silk Fabrics. Fireproof and Waterproof Dressings, together with the principal machinery employed. Translated from the Third German Edition of Friedrich Polleyn. Demy 8vo. 280 pp. Sixty Illustrations. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. abroad.)

THE CHEMICAL TECHNOLOGY OF TEXTILE FIBRES; Their Origin, Structure, Preparation, Washing, Bleaching, Dyeing, Printing and Dressing. By Dr. Georg von Georgievics. Translated from the German by Charles Salter. 320 pp. Forty-seven Illustrations. Royal 8vo. Price 10s. 6d. net. (Post free, 11s. home; 11s. 3d. abroad.)

POWER-LOOM WEAVING AND YARN NUMBERING, According to Various Systems, with Conversion Tables. Translated from the German of Anthon Gruner. **With Twenty-six Diagrams in Colours.** 150 pp. Crown 8vo. Price 7s. 6d. net. (Post free, 7s. 9d. home; 8s. abroad.)

TEXTILE RAW MATERIALS AND THEIR CONVERSION INTO YARNS. (The Study of the Raw Materials and the Technology of the Spinning Process.) By Julius Zipser. Translated from German by Charles Salter. 302 Illustrations. 500 pp. Demy 8vo. Price 10s. 6d. net. (Post free, 11s. home; 11s. 6d. abroad.)

For contents of these books, see List II.

GRAMMAR OF TEXTILE DESIGN. By H. Nisbet, Weaving and Designing Master, Bolton Municipal Technical School. Demy 8vo. 280 pp. 490 Illustrations and Diagrams. Price 6s. net. (Post free, 6s. 4d. home; 6s. 6d. abroad.)

ART NEEDLEWORK AND DESIGN. POINT LACE. A Manual of Applied Art for Secondary Schools and Continuation Classes. By M. E. Wilkinson. Oblong quarto. With 22 Plates. Bound in Art Linen. Price 3s. 6d. net. (Post free, 3s. 10d. home; 4s. abroad.)

HOME LACE-MAKING. A Handbook for Teachers and Pupils. By M. E. W. Milroy. Crown 8vo. 64 pp. With 3 Plates and 9 Diagrams. Price 1s. net. (Post free, 1s. 3d. home; 1s. 4d. abroad.)

THE CHEMISTRY OF HAT MANUFACTURING. Lectures delivered before the Hat Manufacturers' Association. By Watson Smith, F.C.S., F.I.C. Revised and Edited by Albert Shonk. Crown 8vo. 132 pp. 16 Illustrations. Price 7s. 6d. net. (Post free, 7s. 9d. home; 7s. 10d. abroad.)

THE TECHNICAL TESTING OF YARNS AND TEXTILE FABRICS. With Reference to Official Specifications. Translated from the German of Dr. J. Herzfeld. Second Edition. Sixty-nine Illustrations. 200 pp. Demy 8vo. Price 10s. 6d. net. (Post free, 10s. 10d. home; 11s. abroad.)

DECORATIVE AND FANCY TEXTILE FABRICS. By R. T. Lord. For Manufacturers and Designers of Carpets, Damask, Dress and all Textile Fabrics. 200 pp. Demy 8vo. 132 Designs and Illustrations. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. abroad.)

THEORY AND PRACTICE OF DAMASK WEAVING. By H. Kinzer and K. Walter. Royal 8vo. Eighteen Folding Plates. Six Illustrations. Translated from the German. 110 pp. Price 8s. 6d. net. (Post free, 9s. home; 9s. 6d. abroad.)

FAULTS IN THE MANUFACTURE OF WOOLLEN GOODS AND THEIR PREVENTION. By Nicolas Reiser. Translated from the Second German Edition. Crown 8vo. Sixty-three Illustrations. 170 pp. Price 5s. net. (Post free, 5s. 4d. home; 5s. 6d. abroad.)

SPINNING AND WEAVING CALCULATIONS, especially relating to Woollens. From the German of N. Reiser. Thirty-four Illustrations. Tables. 160 pp. Dem. 8vo. 1904. Price 10s. 6d. net. (Post free, 10s. 10d. home; 11s. abroad.)

ANALYSIS OF WOVEN FABRICS. By A. F. Barker and E. Midgley. Demy 8vo. About 200 pages. [*In the press.*

WATERPROOFING OF FABRICS. By Dr. S. Mierzinski. Crown 8vo. 104 pp. 29 Illus. Price 5s. net. (Post free, 5s. 3d. home; 5s. 4d. abroad.)

HOW TO MAKE A WOOLLEN MILL PAY. By John Mackie. Crown 8vo. 76 pp. Price 3s. 6d. net. (Post free, 3s. 9d. home; 3s. 10d. abroad.)

YARN AND WARP SIZING IN ALL ITS BRANCHES. Translated from the German of Carl Kretschmar. Royal 8vo. 123 Illustrations. 150 pp. Price 10s. 6d. net. (Post free, 10s. 10d. home; 11s. abroad.)

(*For "Textile Soaps and Oils" see p.* 7.)

(Dyeing, Colour Printing, Matching and Dye-stuffs.)

THE COLOUR PRINTING OF CARPET YARNS. Manual for Colour Chemists and Textile Printers. By David Paterson, F.C.S. Seventeen Illustrations. 136 pp. Demy 8vo. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. abroad.)

THE SCIENCE OF COLOUR MIXING. A Manual intended for the use of Dyers, Calico Printers and Colour Chemists. By David Paterson, F.C.S. Forty-one Illustrations. **Five Coloured Plates, and Four Plates showing Eleven Dyed Specimens of Fabrics.** 132 pp. Demy 8vo. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. abroad.)

DYERS' MATERIALS: An Introduction to the Examination, Evaluation and Application of the most important Substances used in Dyeing, Printing, Bleaching and Finishing. By Paul Heerman, Ph.D. Translated from the German by A. C. Wright, M.A. (Oxon)., B.Sc. (Lond.). Twenty-four Illustrations. Crown 8vo. 150 pp. Price 5s. net. (Post free, 5s. 4d. home; 5s. 6d. abroad.)

COLOUR MATCHING ON TEXTILES. A Manual intended for the use of Students of Colour Chemistry, Dyeing and Textile Printing. By David Paterson, F.C.S. Coloured Frontispiece. Twenty-nine Illustrations and **Fourteen Specimens of Dyed Fabrics.** Demy 8vo. 132 pp. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. abroad.)

COLOUR: A HANDBOOK OF THE THEORY OF COLOUR. By George H. Hurst, F.C.S. **With Ten Coloured Plates** and Seventy-two Illustrations. 160 pp. Demy 8vo. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. abroad.)

For contents of these books, see List II.

Reissue of
THE ART OF DYEING WOOL, SILK AND COTTON. Translated from the French of M. Hellot, M. Macquer and M. le Pileur D'Apligny. First Published in English in 1789. Six Plates. Demy 8vo. 446 pp. Price 5s. net. (Post free, 5s. 6d. home; 6s. abroad.)

THE CHEMISTRY OF DYE-STUFFS. By Dr. Georg von Georgievics. Translated from the Second German Edition. 412 pp. Demy 8vo. Price 10s. 6d. net. (Post free, 11s. home; 11s. 6d. abroad.)

THE DYEING OF COTTON FABRICS: A Practical Handbook for the Dyer and Student. By Franklin Beech, Practical Colourist and Chemist. 272 pp. Forty-four Illustrations of Bleaching and Dyeing Machinery. Demy 8vo. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. abroad.)

THE DYEING OF WOOLLEN FABRICS. By Franklin Beech, Practical Colourist and Chemist. Thirty-three Illustrations. Demy 8vo. 228 pp. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. abroad.)

(Silk Manufacture.)

SILK THROWING AND WASTE SILK SPINNING. By Hollins Rayner. Demy 8vo. 170 pp. 117 Illus. Price 5s. net. (Post free, 5s. 4d. home; 5s. 6d. abroad.)

(Bleaching and Bleaching Agents.)

A PRACTICAL TREATISE ON THE BLEACHING OF LINEN AND COTTON YARN AND FABRICS. By L. Tailfer, Chemical and Mechanical Engineer. Translated from the French by John Geddes McIntosh. Demy 8vo. 303 pp. Twenty Illus. Price 12s. 6d. net. (Post free, 13s. home; 13s. 6d. abroad.)

MODERN BLEACHING AGENTS AND DETERGENTS. By Professor Max Bottler. Translated from the German. Crown 8vo. 16 Illustrations. 160 pages. Price 5s. net. (Post free, 5s. 3d. home; 5s. 6d. abroad.)

(Cotton Spinning, Cotton Waste and Cotton Combing.)

COTTON SPINNING (First Year). By Thomas Thornley, Spinning Master, Bolton Technical School. 160 pp. 84 Illustrations. Crown 8vo. Second Impression. Price 3s. net. (Post free, 3s. 4d. home; 3s. 6d. abroad.)

COTTON SPINNING (Intermediate, or Second Year). By T. Thornley. 2nd. Impression. 180 pp. 70 Illus. Crown 8vo. Price 5s. net. (Post free, 5s. 4d. home; 5s. 6d. abroad.)

COTTON SPINNING (Honours, or Third Year). By T. Thornley. 216 pp. 74 Illustrations. Crown 8vo. Second Edition. Price 5s. net. (Post free, 5s. 4d. home; 5s. 6d. abroad.)

COTTON COMBING MACHINES. By Thos. Thornley, Spinning Master, Technical School, Bolton. Demy 8vo. 117 Illustrations. 300 pp. Price 7s. 6d. net. (Post free, 8s. home; 8s. 6d. abroad.)

COTTON WASTE: Its Production, Characteristics Regulation, Opening, Carding, Spinning and Weaving. By Thomas Thornley. Demy 8vo. 286 pages. 60 Illustrations. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. abroad.)

THE RING SPINNING FRAME: GUIDE FOR OVERLOOKERS AND STUDENTS. By N. Booth. Crown 8vo. 76 pages. Price 3s. net. (Post free, 3s. 3d. home; 3s. 6d. abroad.)

(Flax, Hemp and Jute Spinning.)

MODERN FLAX, HEMP AND JUTE SPINNING AND TWISTING. A Practical Handbook for the use of Flax, Hemp and Jute Spinners, Thread, Twine and Rope Makers. By Herbert R. Carter, Mill Manager, Textile Expert and Engineer, Examiner in Flax Spinning to the City and Guilds of London Institute. Demy 8vo. 1907. With 92 Illustrations. 200 pp. Price 7s. 6d. net. (Post free, 7s. 9d. home; 8s. abroad.)

(Collieries and Mines.)

RECOVERY WORK AFTER PIT FIRES. By Robert Lamprecht, Mining Engineer and Manager. Translated from the German. Illustrated by Six large Plates, containing Seventy-six Illustrations. 175 pp. Demy 8vo. Price 10s. 6d. net. (Post free, 10s. 10d. home; 11s. abroad.)

VENTILATION IN MINES. By Robert Wabner, Mining Engineer. Translated from the German. Royal 8vo. Thirty Plates and Twenty-two Illustrations. 240 pp. Price 10s. 6d. net. (Post free, 11s. home; 11s. 3d. abroad.)

HAULAGE AND WINDING APPLIANCES USED IN MINES. By Carl Volk. Translated from the German. Royal 8vo. With Six Plates and 148 Illustrations. 150 pp. Price 8s. 6d. net. (Post free, 9s. home; 9s. 3d. abroad.)

THE ELECTRICAL EQUIPMENT OF COLLIERIES. By W. Galloway Duncan, Electrical and Mechanical Engineer, Member of the Institution of Mining Engineers, Head of the Government School of Engineering, Dacca, India; and David Penman, Certificated Colliery Manager, Lecturer in Mining to Fife County Committee. Demy 8vo. 310 pp. 155 Illus. and Diagrams. Price 10s. 6d. net. (Post free, 11s. home; 11s. 3d. abroad.)

(Dental Metallurgy.)

DENTAL METALLURGY: MANUAL FOR STUDENTS AND DENTISTS. By A. B. Griffiths, Ph.D. Demy 8vo. Thirty-six Illustrations. 200 pp. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. abroad.)

For contents of these books, see Lists II and III.

(Engineering, Smoke Prevention and Metallurgy.)

THE PREVENTION OF SMOKE. Combined with the Economical Combustion of Fuel. By W. C. Popplewell, M.Sc., A.M. Inst., C.E., Consulting Engineer. Forty-six Illustrations. 190 pp. Demy 8vo. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. 3d. abroad.)

GAS AND COAL DUST FIRING. A Critical Review of the Various Appliances Patented in Germany for this purpose since 1885. By Albert Pütsch. 130 pp. Demy 8vo. Translated from the German. With 103 Illustrations. Price 5s. net. (Post free, 5s. 4d. home; 5s. 6d. abroad.)

THE HARDENING AND TEMPERING OF STEEL IN THEORY AND PRACTICE. By Fridolin Reiser. Translated from the German of the Third Edition. Crown 8vo. 120 pp. Price 5s. net. (Post free, 5s. 3d. home; 5s. 4d. abroad.)

SIDEROLOGY: THE SCIENCE OF IRON (The Constitution of Iron Alloys and Slags). Translated from German of Hanns Freiherr v. Jüptner. 350 pp. Demy 8vo. Eleven Plates and Ten Illustrations. Price 10s. 6d. net. (Post free, 11s. home; 11s. 6d. abroad.)

EVAPORATING, CONDENSING AND COOLING APPARATUS. Explanations, Formulæ and Tables for Use in Practice. By E. Hausbrand, Engineer. Translated by A. C. Wright, M.A. (Oxon.), B.Sc., (Lond.). With Twenty-one Illustrations and Seventy-six Tables. 400 pp. Demy 8vo. Price 10s. 6d. net. (Post free, 11s. home; 11s. 6d. abroad.)

(The "Broadway" Series of Engineering Handbooks.)

One Uniform Size: Narrow Crown 8vo. (Pocket Size.)

Volume I.—**ELEMENTARY PRINCIPLES OF REINFORCED CONCRETE CONSTRUCTION.** By Ewart S. Andrews, B.Sc. Eng. (Lond.). 200 pages. With 57 Illustrations. Numerous Tables and Worked Examples. Price 3s. net. (Post free, 3s. 3d. home; 3s. 6d. abroad.)

Volume II.—**GAS AND OIL ENGINES.** By A. Kirschke. Translated and Revised from the German, and adapted to British practice. 160 pages. 55 Illustrations. Price 3s. net. (Post free, 3s. 3d. home; 3s. 6d. abroad.)

Volume III. — **IRON AND STEEL CONSTRUCTIONAL WORK.** By K. Schindler. Translated and Revised from the German, and adapted to British practice. 140 pages. 115 Illustrations. Price 3s. 6d. net. (Post free, 3s. 9d. home; 4s. abroad.)

Volume IV.—**TOOTHED GEARING.** By G. T. White, B.Sc. (Lond.). 220 pages. 136 Illustrations. Price 3s. 6d. net. (Post free, 3s. 9d. home; 4s. abroad.)

Volume V.—**STEAM TURBINES**: Their Theory and Construction. By H. Wilda. Translated from the German; Revised and adapted to British practice. 200 pages. 104 Illustrations. Price 3s. 6d. net. (Post free, 3s. 9d. home; 4s. abroad.)

Volume VI.—**CRANES AND HOISTS**. Their Construction and Calculation. By H. Wilda. Translated from the German; revised and adapted to British practice. 168 pages. 399 Illustrations. Price 3s. 6d. net. (Post free, 3s. 9d. home; 4s. abroad.) [*Just published.*

Volume VII.—**FOUNDRY MACHINERY**. By E. Treiber. Translated from the German; revised and adapted to British practice. 148 pages. 51 Illustrations. Price 3s. 6d. net. (Post free, 3s. 9d. home; 4s. abroad.) [*Just published.*

Volume VIII.—**MOTOR CAR MECHANISM**. By W. E. Dommett, A.M.I.A.E.E. 200 pages. 102 Illustrations. Price 3s. 6d. net. (Post free, 3s. 9d. home; 4s. abroad.) [*Just published.*

Volume IX.—**ELEMENTARY PRINCIPLES OF ILLUMINATION AND ARTIFICIAL LIGHTING.** By A. Blok, B.Sc., A.M.I.E.E. Fully illustrated. [*In the press.*

[IN PREPARATION.]

THE CALCULUS FOR ENGINEERS. By E. S. Andrews, B.Sc. Eng. (Lond.), and H. Bryon Heywood, D.Sc.

HYDRAULICS. By E. H. Sprague, A.M.I.C.E.

LAND SURVEYING. By M. T. Ormsby, M.I.C.E.I.

PORTLAND CEMENT. Its Properties and Manufacture. By P. C. H. West, F.C.S.

DESIGN OF MACHINE TOOLS. By G. W. Burley.

LATHES. By G. W. Burley.

REINFORCED CONCRETE IN PRACTICE. By Alban H. Scott, M.S.A., M.C.I.

BRIDGE FOUNDATIONS. By W. Burnside, M.I.C.E.

WORKSHOP MANAGEMENT. By J. Batey.

CALCULATIONS FOR A STEEL FRAME BUILDING. By W. C. Cocking, M C.I.

GEAR CUTTING. By G. T. White, B.Sc. (Lond.).

MODERN GAS WORKS PRACTICE. By Alwyne Meade, A.M.I.E.E.

STEAM BOILERS AND COMBUSTION. By J. Batey.

(Sanitary Plumbing, Electric Wiring, Metal Work, etc.)

EXTERNAL PLUMBING WORK. A Treatise on Lead Work for Roofs. By John W. Hart, R.P.C. 180 Illustrations. 272 pp. Demy 8vo. Second Edition Revised. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. abroad.)

For contents of these books, see List III.

HINTS TO PLUMBERS ON JOINT WIPING, PIPE BENDING AND LEAD BURNING. Third Edition, Revised and Corrected, By JOHN W. HART, R.P.C. 184 Illustrations. 313 pp. Demy 8vo. Price 7s. 6d. net. (Post free, 8s. home; 8s. 6d. abroad.)

SANITARY PLUMBING AND DRAINAGE. By JOHN W. HART. Demy 8vo. With 208 Illustrations. 250 pp. 1904. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. abroad.)

ELECTRIC WIRING AND FITTING. By SYDNEY F. WALKER, R.N., M.I.E.E., M.I.Min.E., A.M.Inst.C.E., etc., etc. Crown 8vo. 150 pp. With Illustrations and Tables. Price 5s. net. (Post free, 5s. 3d. home; 5s. 6d. abroad.)

THE PRINCIPLES AND PRACTICE OF DIPPING, BURNISHING, LACQUERING AND BRONZING BRASS WARE. By W. NORMAN BROWN. 48 pp. Crown 8vo. Price 3s. net. (Post free, 3s. 3d. home and abroad.)

THE DEVELOPMENT OF THE INCANDESCENT ELECTRIC LAMP. By G. BASIL BARHAM, A.M.I.E.E. Demy 8vo. 200 pages. 2 Plates, 25 Illustrations and 10 Tables. Price 5s. net. (Post free, 5s. 4d. home; 5s. 6d. abroad.)

WIRING CALCULATIONS FOR ELECTRIC LIGHT AND POWER INSTALLATIONS. A Practical Handbook containing Wiring Tables, Rules, and Formulæ for the Use of Architects, Engineers, Mining Engineers, and Electricians, Wiring Contractors and Wiremen, etc. By G. W. LUMMIS PATERSON. Crown 8vo. 96 pages. 35 Tables. Price 5s. net. (Post free, 5s. 3d. home; 5s. 6d. abroad.)

A HANDBOOK ON JAPANNING. For Ironware, Tinware, and Wood, etc. By WILLIAM NORMAN BROWN. Second Edition. 70 pages. 13 Illustrations. Crown 8vo. Price 3s. 6d. net. (Post free, 3s. 9d. home; 4s. abroad.)

THE PRINCIPLES OF HOT WATER SUPPLY. By JOHN W. HART, R.P.C. With 129 Illustrations. 177 pp. Demy 8vo. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. abroad.)

(Brewing and Botanical.)

HOPS IN THEIR BOTANICAL, AGRICULTURAL AND TECHNICAL ASPECT, AND AS AN ARTICLE OF COMMERCE. By EMMANUEL GROSS, Professor at the Higher Agricultural College, Tetschen-Liebwerd. Translated from the German. 78 Illus. 340pp. Demy 8vo. Price 10s. 6d. net. (Post free, 11s. home; 11s. 6d. abroad.)

INSECTICIDES, FUNGICIDES AND WEEDKILLERS. By E. BOURCART, D.Sc. Translated from the French. Revised and Adapted to British Standards and Practice. Demy 8vo. 450 pages, 83 Tables, and 12 Illustrations. Price 12s. 6d. net. (Post free, 13s. home; 13s. 6d. abroad.)

(For Agricultural Chemistry, see p. 9.)

(Wood Products, Timber and Wood Waste.)

WOOD PRODUCTS: DISTILLATES AND EXTRACTS. By P. Dumesny, Chemical Engineer, Expert before the Lyons Commercial Tribunal, Member of the International Association of Leather Chemists; and J. Noyer. Translated from the French by Donald Grant. Royal 8vo. 320 pp. 103 Illustrations and Numerous Tables. Price 10s. 6d. net. (Post free, 11s. home; 11s. 6d. abroad.)

TIMBER: A Comprehensive Study of Wood in all its Aspects (Commercial and Botanical), showing the different Applications and Uses of Timber in Various Trades, etc. Translated from the French of Paul Charpentier. Royal 8vo. 437 pp. 178 Illustrations. Price 12s. 6d. net. (Post free, 13s. home; 14s. abroad.)

THE UTILISATION OF WOOD WASTE. Translated from the German of Ernst Hubbard. Crown 8vo. 192 pp. 50 Illus. Price 5s. net. (Post free, 5s. 4d. home; 5s. 6d. abroad.)

(*See also Utilisation of Waste Products, p.* 9.)

(Building and Architecture.)

ORNAMENTAL CEMENT WORK. By Oliver Wheatley. Demy 8vo. 83 Illustrations. 128 pp. Price 5s. net. (Post free, 5s. 4d. home; 5s. 6d. abroad.)

THE PREVENTION OF DAMPNESS IN BUILDINGS; with Remarks on the Causes, Nature and Effects of Saline, Efflorescences and Dry-rot, for Architects, Builders, Overseers, Plasterers, Painters and House Owners. By Adolf Wilhelm Keim. Translated from the German of the second revised Edition by M. J. Salter, F.I.C., F.C.S. Eight Coloured Plates and Thirteen Illustrations. Crown 8vo. 115 pp. Price 5s. net. (Post free, 5s. 3d. home; 5s. 4d. abroad.)

HANDBOOK OF TECHNICAL TERMS USED IN ARCHITECTURE AND BUILDING, AND THEIR ALLIED TRADES AND SUBJECTS. By Augustine C. Passmore. Demy 8vo. 380 pp. Price 7s. 6d. net. (Post free, 8s. home; 8s. 6d. abroad.)

(Foods, Drugs and Sweetmeats.)

FOOD AND DRUGS. By E. J. Parry, B.Sc., F.I.C., F.C.S.

Volume I. The Analysis of Food and Drugs (Chemical and Microscopical). Royal 8vo. 724 pp. Price 21s. net. (Post free, 21s. 6d. home; 22s. 6d. British Colonies; 23s. 3d. other Foreign Countries.)

Volume II. The Sale of Food and Drugs Acts, 1875-1907. Royal 8vo. 184 pp. Price 7s. 6d. net. (Post free, 7s. 10d. home; 8s. abroad.)

For contents of these books, see List III.

THE MANUFACTURE OF PRESERVED FOODS AND SWEETMEATS. By A. HAUSNER. With Twenty-eight Illustrations. Translated from the German of the third enlarged Edition. Second English Edition. Crown 8vo. 225 pp. Price 7s. 6d. net. (Post free, 7s. 9d. home; 7s. 10d. abroad.)

RECIPES FOR THE PRESERVING OF FRUIT, VEGETABLES AND MEAT. By E. WAGNER. Translated from the German. Crown 8vo. 125 pp. With 14 Illustrations. Price 5s. net. (Post free, 5s. 3d. home; 5s. 4d. abroad.)

(Dyeing Fancy Goods.)

THE ART OF DYEING AND STAINING MARBLE, ARTIFICIAL STONE, BONE, HORN, IVORY AND WOOD, AND OF IMITATING ALL SORTS OF WOOD. A Practical Handbook for the Use of Joiners, Turners, Manufacturers of Fancy Goods, Stick and Umbrella Makers, Comb Makers, etc. Translated from the German of D. H. SOXHLET, Technical Chemist. Crown 8vo. 168 pp. Price 5s. net. (Post free, 5s. 3d. home; 5s. 4d. abroad.)

(Celluloid.)

CELLULOID: Its Raw Material, Manufacture, Properties and Uses. A Handbook for Manufacturers of Celluloid and Celluloid Articles, and all Industries using Celluloid; also for Dentists and Teeth Specialists. By Dr. Fr. BÖCKMANN, Technical Chemist. Translated from the Third Revised German Edition. Crown 8vo. 120 pp. With 49 Illustrations. Price 5s. net. (Post free, 5s. 3d. home; 5s. 4d. abroad.)

(Lithography, Printing and Engraving.)

ART OF LITHOGRAPHY. By G. T. RHODES. [*In the press.*

PRINTERS' AND STATIONERS' READY RECKONER AND COMPENDIUM. Compiled by VICTOR GRAHAM. Crown 8vo. 112 pp. 1904. Price 3s. 6d. net. (Post free, 3s. 9d. home; 3s. 10d. abroad.)

ENGRAVING FOR ILLUSTRATION. HISTORICAL AND PRACTICAL NOTES. By J. KIRKBRIDE. 72 pp. Two Plates and 6 Illustrations. Crown 8vo. Price 2s. 6d. net. (Post free, 2s. 9d. home; 2s. 10d. abroad.)

(*For Printing Inks, see p.* 4.)

(Bookbinding.)

PRACTICAL BOOKBINDING. By PAUL ADAM. Translated from the German. Crown 8vo. 180 pp. 127 Illustrations. Price 5s. net. (Post free, 5s. 4d. home; 5s. 6d. abroad.

(Sugar Refining.)

THE TECHNOLOGY OF SUGAR: Practical Treatise on the Modern Methods of Manufacture of Sugar from the Sugar Cane and Sugar Beet. By JOHN GEDDES McINTOSH. Second Revised and Enlarged Edition. Demy 8vo. Fully Illustrated. 436 pp. Seventy-six Tables. 1906. Price 10s. 6d. net. (Post free, 11s. home; 11s. 6d. abroad.)

(*See "Evaporating, Condensing, etc., Apparatus," p.* 19.)

(Emery.)

EMERY AND THE EMERY INDUSTRY. Translated from the German of A. HAENIG. Crown 8vo. 45 Illus. 104 pp. Price 5s. net. (Post free, 5s. 3d. home; 5s. 6d. abroad.)

(Libraries and Bibliography.)

CLASSIFIED GUIDE TO TECHNICAL AND COMMERCIAL BOOKS. Compiled by EDGAR GREENWOOD. Demy 8vo. 224 pp. 1904. Being a Subject-list of the Principal British and American Books in Print; giving Title, Author, Size, Date, Publisher and Price. Price 5s. net. (Post free, 5s. 4d. home; 5s. 6d. abroad.)

HANDBOOK TO THE TECHNICAL AND ART SCHOOLS AND COLLEGES OF THE UNITED KINGDOM. Containing particulars of nearly 1,000 Technical, Commercial and Art Schools throughout the United Kingdom. With full particulars of the courses of instruction, names of principals, secretaries, etc. Demy 8vo. 150 pp. Price 3s. 6d. net. (Post free, 3s. 10d. home; 4s. abroad.)

THE LIBRARIES, MUSEUMS AND ART GALLERIES YEAR BOOK, 1910-11. Being the Third Edition of Greenwood's "British Library Year Book". Edited by ALEX. J. PHILIP. Demy 8vo. 286 pp. Price 5s. net. (Post free, 5s. 4d. home; 5s. 6d. abroad.)

THE PLUMBING, HEATING AND LIGHTING ANNUAL FOR 1911. The Trade Reference Book for Plumbers, Sanitary, Heating and Lighting Engineers, Builders' Merchants, Contractors and Architects. Including the translation of Hermann Recknagel's "Kalender für Gesundheits-Techniker," Handbook for Heating, Ventilating, and Domestic Engineers, of which Scott, Greenwood & Son have purchased the sole right for the English Language. Quarto. Bound in cloth and gilt lettered. Price 3s. net. (Post free, 3s. 4d. home; 3s. 8d. abroad.)

SCOTT, GREENWOOD & SON,
Technical Book and Trade Journal Publishers,
8 BROADWAY, LUDGATE, LONDON, E.C.

Telegraphic Address, "Printeries, Cent.-London". *October*, 1913.