THE ANALYSIS OF DYESTUFFS.

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THE BLEACHING, DYEING, AND CHEMICAL TECHNOLOGY OF TEXTILE FIBRES.

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THE

ANALYSIS OF DYESTUFFS

AND THEIR

IDENTIFICATION IN DYED AND COLOURED MATERIALS, LAKE-PIGMENTS, FOODSTUFFS, ETC.

BY

ARTHUR G. GREEN, M.Sc., F.R.S., F.I.C.
DIRECTOR OF RESEARCH, BRITISH DYESTUFFS CORPN. (BLACKLEY);
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With 31 Analytical Tables.

THIRD EDITION,
with "Key to Trade Designations,"
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PREFACE TO THE THIRD EDITION.

SINCE the first edition of this work went to press in the Autumn of 1914 the dyestuff industry has experienced considerable changes. As the result of war conditions very many dyestuffs, previously only produced in Germany, are now manufactured in Great Britain. A similar development has also taken place in the United States and to a smaller extent in some other countries. By reason of this activity a number of dyestuffs, which for the most part are not actually new, have been brought upon the market under novel designations. Many of these trade names are probably only ephemeral and will eventually give place to the names under which the products were known originally. It has been felt, therefore, that to incorporate them in the text and tables would only encumber the very limited space available without any sufficient advantage. At the same time, in order to provide a guide to those who desire information upon the chemical relationships of such dyestuffs, it has been deemed desirable to insert in the index the most important of them, accompanied by cross references to the products of German origin to which they are equivalent or most nearly related.

With the object of still further facilitating reference, I have also added a "Key to Trade Designations" based upon a table prepared by Dr J. Merritt Matthews and published in the "Colour Trade Journal."

In all other particulars the book is reprinted without alterations.

A. G. G.

MANCHESTER,
February 1920.

PREFACE.

THE great progress in the development of the Artificial Dyestuff Industry, which has marked the past half-century, has brought with it an urgent necessity for systematic methods of analysis capable of being applied not only to dyestuffs in substance but also to all manner of dyed and coloured materials, such as textile fabrics, lake pigments, paper, foodstuffs, etc. Though any desired shade can now be obtained in many different ways, the properties and fastness of the result will be dependent entirely on the dyestuffs selected. Hence arises the need in many industries for analytical investigation and control.

The methods of analysis here presented are for the most part the revised and completed results of a series of investigations conducted by the author, with the assistance of various collaborators, during the past twenty years.[1] The favourable reception accorded to these methods by prominent technologists in this and other countries, and the satisfactory results attendant on their use in the laboratories of the Leeds University and elsewhere, have encouraged the belief that they would prove of utility if introduced to a wider circle of scientific and technical workers. In particular it is hoped that they may afford assistance to the various users of dyestuffs and dyed materials, such as dyers, calico printers, pigment manufacturers, wall-paper printers, and others.

In order to meet the needs of many who are interested in the application of dyestuffs but whose knowledge of the chemistry of the subject is limited, it has been thought desirable to preface the analytical schemes by a short theoretical introduction, especially from the standpoint of dyestuff classification. It is hoped thereby

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[1] *J. Soc. Chem. Ind.*, 1893, p. 3 ; *J. Soc. Dyers and Cols.*, 1905, p. 236 ; 1907, pp. 118, 252 ; 1910, p. 83 ; 1913, p. 226.

to facilitate for such readers the comprehension and successful application of the analytical procedure.

The chapter on the determination of the constitution of azo dyestuffs has been inserted at the special request of chemists specialising in this branch. Whilst the methods employed are those proposed by Witt, Grandmougin, and others, much individual experience and data have been added.

In conclusion, the author desires to express his thanks to the various gentlemen who have collaborated with him, and in particular to acknowledge the valuable services rendered by his assistants, Mr G. H. Frank, M.Sc., and Mr A. E. Woodhead, M.Sc. He is also indebted to the courtesy of many firms of colour manufacturers who have supplied him with samples of dyestuffs and dyed materials, notably the Badische Aniline Co., the Farbenfabriken F. Bayer & Co., the Berlin Aniline Co., Messrs L. Cassella & Co., Messrs R. Geigy & Co., Messrs Kalle, Messrs Meister, Lucius & Brüning, Messrs Read, Holliday & Sons, and the Society of Chemical Industry in Basle.

A. G. G.

THE UNIVERSITY, LEEDS,
April 1915.

CONTENTS.

CHAPTER I.

INTRODUCTION TO DYESTUFF CHEMISTRY.

CHAPTER II.

CLASSIFICATION OF DYESTUFFS.

CHAPTER III.

CLASSIFICATION OF DYESTUFFS (*contd.*).

CHAPTER IV.

ANALYSIS OF COLOURING MATTERS IN SUBSTANCE.

CHAPTER V.

IDENTIFICATION OF DYESTUFFS ON ANIMAL FIBRES.

CHAPTER VI.

IDENTIFICATION OF DYESTUFFS ON VEGETABLE FIBRES.

CHAPTER VII.

ANALYSIS OF INDIGO IN SUBSTANCE AND UPON THE FIBRE.

CHAPTER VIII.

ANALYSIS OF PIGMENTS AND LAKES.

CHAPTER IX.

DETERMINATION OF THE CONSTITUTION OF AZO DYESTUFFS.

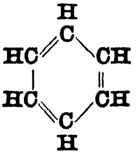
THE ANALYSIS OF DYESTUFFS, COLOURED MATERIALS AND PIGMENTS.

CHAPTER I.

INTRODUCTION TO DYESTUFF CHEMISTRY.

DYESTUFFS, whether of natural or artificial origin, are complex compounds of the element carbon in association with other elements, more especially with hydrogen, nitrogen, oxygen, or sulphur. They belong therefore to the class of bodies termed by chemists "organic compounds," and indeed to that particular division of this class known as "aromatic."

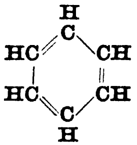
Dyestuffs, like "aromatic" compounds in general, contain their constituent carbon atoms arranged in the form of closed chains. They may be regarded as derived from "closed chain" or "benzenoid" hydrocarbons by the replacement of some of the hydrogen atoms by atoms or atomic groups of other elements. Thus the hydrocarbon benzene, C_6H_6, has the structure,



which for simplicity's sake is frequently written as a plain hexagon. The replacement of certain of the hydrogen atoms in this colourless body by suitable atomic groups gives rise to dyestuffs; and these dyestuffs may contain a single benzene nucleus, or more usually two or more such benzene nuclei united by certain of the atomic groups introduced. Furthermore, the hydrocarbon nuclei which are thus bound together may be those of the same or of different hydrocarbons. In other words, we may regard a dyestuff molecule as consisting of one or more chains of carbon atoms, forming the skeleton of the system, to which are attached various groups of other atoms. Upon the structure and position of these atomic groups the character and properties of the dyestuff mainly depend, just as in the animal kingdom the life of the organism depends upon the specific functions of the nerves, muscles, and other organs attached to the bony skeleton.

Nearly all the artificial dyestuffs, and also all those of natural origin, are derived from one or other of the following hydrocarbons:

Benzene, C_6H_6, *i.e.*



usually contracted to

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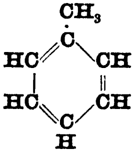
Toluene or **Methylbenzene**, C_7H_8, *i.e.*



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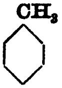

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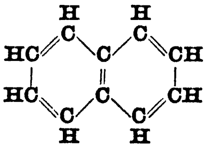
(Also to a smaller extent **xylene** or **dimethylbenzene**, C_8H_{10}.)

Naphthalene, $C_{10}H_8$, *i.e.*



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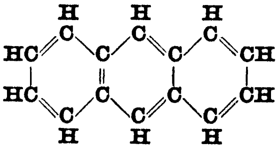
Anthracene, $C_{14}H_{10}$, *i.e.*



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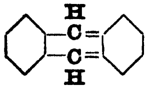
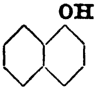


These hydrocarbons are contained, together with a great variety of other substances, in coal-tar, the black viscid fluid obtained as a bye-product in the manufacture of illuminating gas or of metallurgical coke. They are isolated from this material by making use of the differences in their boiling-points and other physical properties. Upon submitting coal-tar to distillation, a distillate is obtained the first portion of which contains benzene and its homologues, toluene and the xylenes. The next fraction is rich in the hydrocarbon naphthalene; whilst the portion passing over last contains anthracene. The two latter substances, being solids, crystallise out from the oils on cooling. The raw hydrocarbons obtained from these several fractions are purified by submitting them to redistillation or crystallisation combined with chemical washing with acids and alkalies. In the pure state, benzene, toluene, and xylene are colourless volatile liquids; naphthalene and anthracene, colourless crystalline solids.

From these starting materials the artificial dyestuffs are built up in successive stages, but we can only take a very cursory glance at these operations. In the first place, the hydrocarbons are converted into so-called "intermediate products," obtained by replacing one or more atoms of hydrogen by simple atomic groups, such as the amido group ($-NH_2$), or hydroxy group ($-OH$). Thus, from benzene is prepared by nitration and reduction amidobenzene or aniline,

from naphthalene is obtained by sulphonation and fusion with caustic soda the hydroxy-naphthalenes or naphthols,



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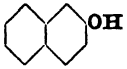
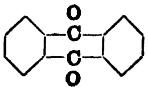


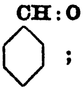
α-Naphthol. β-Naphthol.

From anthracene there is obtained by oxidation anthraquinone,



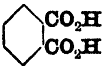
;

from toluene, benzaldehyde,



;

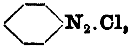
and from naphthalene, phthalic acid,



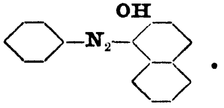
, etc.

The sulphonic group ($-HSO_3$), nitro ($-NO_2$), nitroso ($-NO$), and halogen (Cl or Br) groups are introduced by treatment of the original hydrocarbons or of their amido or hydroxy derivatives with sulphuric acid, nitric acid, nitrous acid, or halogens respectively. Dimethylamido ($-N(CH_3)_2$), diethylamido ($-N(C_2H_5)_2$), and other substituted amido derivatives are obtained by alkylation of the amido compounds; diphenylamine derivatives by causing amido compounds to react with chloro compounds. By the introduction of two or more of the above atomic groups into the hydrocarbon nucleus there are obtained diamines, amidophenols, dihydroxy compounds, naphthylamine sulphonic acids, amidonaphthol sulphonic acids, etc., in which the relative position occupied by the respective groups plays a very important rôle, and isomerism, more especially in the naphthalene series, becomes a factor of great importance.

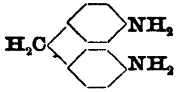
These numerous intermediate compounds, like the parent hydrocarbons from which they are derived, are still for the most part colourless. They are converted into colouring-matters when by further chemical treatment certain other groups of atoms (chromophors) are introduced and a greater complexity of structure obtained. Thus by the action of nitrous acid upon aniline hydrochloride there is formed diazobenzene chloride,



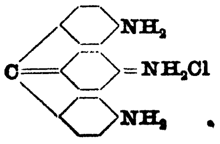
which, also a colourless body, gives upon treatment with β-naphthol, an orange dyestuff (benzeneazonaphthol),



Again, to take another example, if aniline is condensed with formaldehyde, the colourless intermediate product, diamidodiphenylmethane,



is obtained. When this is heated with a further quantity of a salt of aniline in the presence of an oxidising agent, the deep red dyestuff Magenta is produced,



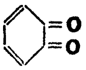
In this dyestuff a single carbon atom derived from the formaldehyde unites together three benzene nuclei.

By making use of these and many other similar methods, it is possible for the colour chemist to build up dyestuff molecules having almost any required structure, and containing the particular atomic groupings necessary to produce the desired properties. It does not lie, however, within the scope of this cursory survey to enter into the methods of dyestuff manufacture, for further particulars of which the reader is referred to the special works on the subject.

Relation between Colour and Chemical Constitution.

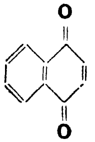
Although the property of colour is usually associated with a certain degree of complexity of molecular structure, this of itself cannot be regarded as the cause of colour manifestation, for many very complex derivatives of "aromatic" hydrocarbons, for example the tannins, are entirely colourless. The first attempt to establish a chemical theory of colour was made by Witt in 1876, who attributed dyeing properties to the simultaneous presence in the compound of two classes of atomic groups, viz. *chromophors*, or groups which predispose to colour (for instance, the nitroso, nitro, or azo groups), and *auxochromes*, or groups which intensify the colour called forth by the chromophor. These latter are the hydroxyl group (OH), the amido group (NH_2), and substituted amido groups. A compound containing a chromophor only was termed a *chromogen*: it might be more or less coloured, but required the introduction of auxochrome groups to render it a dyestuff. Whilst the above theory is not entirely superseded, most chemists at the present day attribute the manifestation of colour and dyeing properties amongst "aromatic" compounds to a peculiar unsaturated condition of the hydrocarbon ring similar to that occurring in the quinones. According to this view, all dyestuffs are "quinonoid" in structure, or capable of existence in a "quinonoid" form. The two quinones derived from benzene have the structure:

and



Parabenzoquinone. Orthobenzoquinone.

whilst those derived from naphthalene have the structure:



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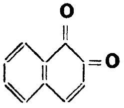
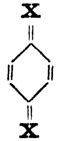
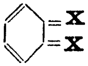


α-Naphthaquinone. β-Naphthaquinone.

Accordingly, upon this hypothesis we may represent all dyestuffs as constituted upon the general type:

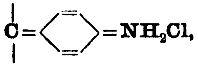


or



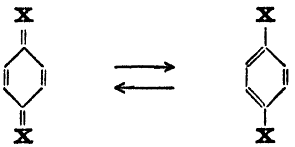
Paraquinonoid. Orthoquinonoid.

or by similar formulæ derived from naphthalene and anthracene. In these formulæ the symbol X stands for simple or complex atomic groups. Thus, for example, in the formula for Magenta, already given, the central nucleus,



is quinonoid; and this group is regarded as the source of colour in all the dyestuffs of the triphenylmethane class. It is therefore the true "chromophor" of this class of colouring-matters.

It is an important fact that many dyestuffs are capable of existence both in a "quinonoid" and a "benzenoid" (non-quinonoid) form, and may change from one form to the other with alteration of conditions (solvent, alkalinity, acidity, temperature, etc.). This transformation is accompanied by a loss or gain of colour, and may be represented by the general expression:

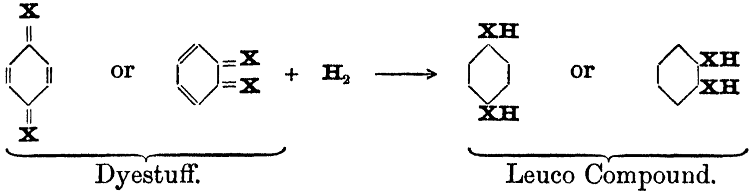


Coloured. Colourless.

This tendency to isomeric change serves to explain many well-known facts, as, for example, the pale colour of picric acid in the solid state contrasted with its much deeper colour upon the fibre; the decolourisation of certain dyestuffs of the triphenylmethane series by alkalies, *e.g.* of Alkali Blue; the red salts of the colourless phenolphthalein; the colourless solutions given by Rhodamine in anhydrous ether or benzene, etc. It has probably also an important bearing upon the fastness of many dyestuffs to light, soap, and other agencies.

LEUCO COMPOUNDS.

It is a well-known peculiarity of most dyestuffs that they readily take up hydrogen with the production of colourless compounds. Whilst in the case of the nitro, nitroso, and azo colours, amido compounds are produced from which the original dyestuffs cannot be regenerated, all other classes of colouring-matters are converted with greater or lesser ease into so-called "leuco compounds." These are substances (usually colourless) containing two atoms of hydrogen more than the original dyestuff from which they are formed, and reconvertible into the latter upon oxidation. These facts receive a ready explanation upon the quinonoid hypothesis, and may be represented by the general expression:



In other words, the reduction of the dyestuffs, as of their prototypes the quinones, gives rise to benzenoid compounds. Only in the case of the anthraquinone dyestuffs are the " leuco " compounds coloured, and this is probably to be accounted for by the presence of two chromophoric groups in dyestuffs of this class, so that the " leuco " compound (the word is here a misnomer) still has a quinonoid structure.

The facility with which the leuco compounds derived from various classes of dyestuffs are reoxidised to the original dyestuff varies with their structure, and is probably dependent upon whether the dyestuff has an *orthoquinonoid* or a *paraquinonoid* constitution.[1] We find, for instance, that the leuco compounds of the indigoid dyestuffs, which must have an *ortho* quinonoid constitution, are

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[1] See A. G. Green, *Proc. Chem. Soc.*, 1892, p. 195; 1896, p. 226; *Rev. Gen. des Mat. Col.*, 1897, p. 269.

readily oxidised by air, whilst those of the triphenylmethane and indamine series, to which only a *para* quinonoid constitution can be ascribed, are stable to atmospheric oxidation and require the application of a stronger oxidising agent, such as chromic acid, persulphuric acid, or permanganic acid, to restore their colour. These differences of behaviour afford valuable assistance in distinguishing between dyestuff classes, and are made use of in the analytical tables which follow in later chapters.

The facility with which different classes of dyestuffs suffer reduction to their leuco compounds is also a variable factor dependent upon specific structure. Thus the triphenylmethane dyestuffs are less easily reduced than the azines, oxazines, or thiazines, but more readily than the phthalein or acridine dyestuffs.[1] In particular, it is found that dyestuffs containing the quinoline group and the thiazol group are only reduced with considerable difficulty, a fact which is conveniently used to differentiate these classes.

Closely related to the leuco compounds are the "*bisulphite*" compounds, a class of bodies which are produced when certain dyestuffs, especially those containing CO groups, are treated with a solution of sodium bisulphite. These compounds have the advantage of being soluble in water even when the dyestuff from which they are derived is insoluble, and as they are readily reconverted into the parent substance upon steaming or treatment with alkalies, they are frequently employed in calico-printing in place of the dyestuff itself. Thus, Alizarine Blue S is the bisulphite compound of the insoluble Alizarine Blue, Gallocyanine BS the bisulphite compound of Gallocyanine. A similar principle is made use of for dyeing and printing, in the employment of alkaline salts of certain leuco compounds in place of the more sparingly soluble dyestuffs. Thus in the indigo and oxazine classes soluble leuco compounds are sold which undergo reoxidation during use. Those dyestuffs of the "sulphide" class which are brought upon the market in a soluble form by admixture with sodium sulphide, may also be regarded as belonging to this category.

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[1] *Cf.* A. G. Rota, *Chem. Zeit.*, 1898, p. 437; *J. Soc. Chem. Ind.*, 1898, p. 798.

CHAPTER II.

CLASSIFICATION OF DYESTUFFS.

WHILST the structural framework of the dyestuff molecule may be regarded as primarily responsible for the existence of colour, the specific properties of the dyestuff, such as shade, affinity for fibres, fastness, and behaviour to reagents, depend largely upon the particular atomic groups with which this framework is clothed. These atomic groups are of two kinds: (*a*) chromophoric groups; (*b*) salt-forming groups, *e.g.* basic, acid, hydroxylic, or sulphide. Whilst the atomic groupings of the first kind determine the *chemical* class to which a particular dyestuff belongs, and hence its behaviour upon reduction and reoxidation, those of the second kind are largely responsible for its *dyeing* properties and the fastness of the dyed material towards acids, alkalies, soap, milling, etc. A dyestuff of almost any chemical class may be given "basic," "acid," or "mordant-dyeing" properties by the introduction of basic, acid, or hydroxylic groups in suitable positions.

From the above it is clear that it is possible to classify dyestuffs by two methods, viz.:—

A. Into *chemical classes* according to the specific chromophor present, or

B. Into *dyeing classes* according to the method of application.

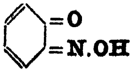
In the pages which follow, the dyestuffs will be regarded from these two points of view in turn; whichever we employ as the primary system of classification, the other may be used for subdivision.

A. CHEMICAL CLASSES.

The following are the most important classes of dyestuffs, arranged according to their constituent chromophors:—

I. **Nitroso Compounds.**—*Typical grouping:*

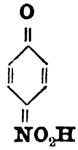
or



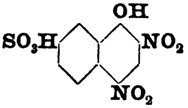
This is a very small class, mainly represented by mordant dyestuffs used in calico-printing, such as Fast or Steam Green (dinitrosoresorcin). Their iron lakes are dark green, the chromium lakes, brown. Upon reduction, the members of this group are converted into colourless amido compounds from which the original dyestuffs cannot be regenerated by oxidation.

II. Nitro Compounds.—*Typical grouping:*

or

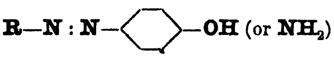


This is also a small class, represented only by yellow dyestuffs having acid properties. The most important member is Naphthol Yellow S, a dinitronaphthol sulphonic acid,

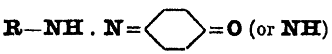


Upon reduction, the nitro dyestuffs, like those of the nitroso class, are converted into colourless amido compounds, incapable of regenerating the original dyestuff upon oxidation. When heated with a solution of sodium or ammonium sulphide the colour first changes to orange, through formation of intermediate nitroamido compounds, before complete reduction ensues. The solid dyestuff usually deflagrates when brought into a flame. Those dyestuffs of this class which do not contain sulphonic groups are readily volatilised by heat, and give a yellow stain when placed against white paper in contact with a hot iron. This may be used as a test for unsulphonated nitro compounds in articles of diet, for which they are sometimes employed.

III. Azo Compounds.—*Typical grouping:*



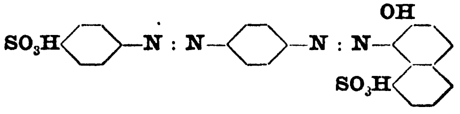
or



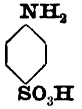
(and ortho compounds of analogous type).

This is a very large class of dyestuffs, far exceeding all others in the number of its representatives, some of which have neutral, some acid, some basic, and some mordant-dyeing properties. It consists of compounds in which two or more hydrocarbon nuclei are united by the azo group ($-N_2-$). One, two, three, or occasionally four of these groups may be present, the molecular complexity increasing with their number. The azo compounds of simpler structure are usually yellow to red in colour; those of more complex constitution, violet to blue and black. Amongst analogously constituted compounds with the same number of azo groups, those containing naphthalene nuclei have a darker colour than those containing benzene nuclei. Lake formation also tends to increase the depth of shade: thus the red Chromotropes become dark blue to black upon conversion into chromium lakes.

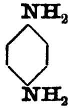
By reduction, the azo dyestuffs, after intermediate formation of very unstable hydrazo compounds, are completely destroyed, being broken up between the double nitrogen groups into two or more colourless amido compounds. Thus, to take an example, Crocein Scarlet 3B, which has the formula



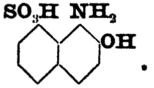
gives upon reduction parasulphanilic acid,



paraphenylenediamine,



and amidobetanaphthol sulphonic acid,



From the products of resolution, the constitution of the azo dyestuff can be deduced, and this procedure has become a valuable means for ascertaining the structure of dyestuffs of this class. Upon the amount of hydrogen consumed during reduction there has also been based an accurate method of estimating azo dyestuffs either in solution or upon the fibre, consisting in titration with a standard solution of titanium trichloride.[1] Each azo group consumes four atoms of hydrogen for complete reduction, equivalent to four molecules of $TiCl_3$.

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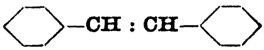
[1] Knecht, *J. Soc. Dyers and Cols.*, 1903, p. 169; 1904, p. 97; 1905, p. 292.

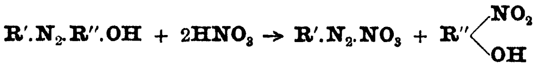
In the case of the azo dyestuffs belonging to the stilbene class, *i.e.* azo dyestuffs containing the diphenylethylene group,



the intermediate hydrazo compounds are more stable. These dyestuffs are consequently not broken up at once, but are first reduced to intermediate leuco compounds which reoxidise to the original dyestuff in air, and only upon more prolonged action of the reducing agent give stable amido compounds (diamidostilbenedisulphonic acid, etc.).

Azo dyestuffs containing a second chromophor, such as the azosafranine colours (Indoin Blue, Janus Blue, Janus Green, etc.) or those of the azothiazol class (Primuline Red, Erica, etc.), give on reduction the parent amido compound belonging to the azine or thiazol class (*e.g.* Safranine or Primuline Yellow) or its leuco compound.

Oxidising agents also effect a splitting of azo dyestuffs into two or more products, though in this case the azo groups remain intact.[1] Thus upon dissolving hydroxy azo dyestuffs in cold fuming nitric acid, a diazo salt and a nitrophenol are produced according to the general equation:



$$R'.N_2.R''.OH + 2HNO_3 \rightarrow R'.N_2.NO_3 + R''\begin{cases} NO_2 \\ OH \end{cases}$$

When the phenolic residue contains an easily replaceable hydrogen atom or sulphonic group, a second nitro group may be simultaneously introduced. Conclusions can be drawn as to the structure of the dyestuff, by identification of the nitrophenol obtained, and by examining the colour reactions given by the diazo salt upon treatment with various phenols in alkaline solution. The method is particularly useful as a supplement to the reduction process, in ascertaining the constitution of azo compounds containing naphtholsulphonic acid residues.

Many azo dyestuffs dissolve in concentrated sulphuric acid with very characteristic colours, which are different from those of their aqueous or alcoholic solutions. This reaction can frequently be used to characterise individual members of a series or to distinguish mixtures. Though no rule can be laid down, the colour of the solution in concentrated sulphuric acid is largely influenced by the

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[1] Meldola and Morgan, *Trans. Chem. Soc.*, 55, 608 ; 65, 841 ; O. Schmidt, *Ber.*, 38, 3201 ; *J. prakt. Chem.*, 1912, p. 235 ; Mathewson, *Chem. News*, 1913, p. 265.

position of the sulphonic groups in the molecule. A remarkable illustration of this is furnished by the three scarlet dyestuffs: Crocein Scarlet, Brilliant Scarlet, and Biebrich Scarlet, which are all disulphonic acids of the same azo compound, differing only in the position of the sulphonic groups:

Crocein Scarlet,

$$C_6H_4(SO_3H).N_2.C_6H_4.N_2.C_{10}H_5(OH)SO_3H.$$

Brilliant Scarlet,

$$C_6H_5.N_2.C_6H_4.N_2.C_{10}H_4(OH)(SO_3H)_2.$$

Biebrich Scarlet,

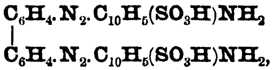
$$C_6H_4(SO_3H).N_2.C_6H_3(SO_3H).N_2.C_{10}H_6(OH).$$

These dyestuffs all dissolve in water and dye with nearly the same colour, but in concentrated sulphuric acid the first gives a blue solution, the second a violet, and the third a green.

"Acid" azo dyestuffs containing amido groups, are usually more or less sensitive to dilute mineral acids. Thus Methyl Orange,

$$C_6H_4(SO_3H).N_2.C_6H_4.N(CH_3)_2,$$

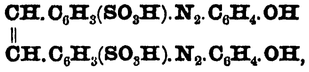
is changed to red, and Congo Red,



$$\begin{array}{l} C_6H_4.N_2.C_{10}H_5(SO_3H)NH_2 \\ | \\ C_6H_4.N_2.C_{10}H_5(SO_3H)NH_2, \end{array}$$

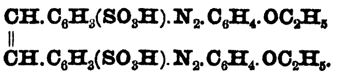
becomes blue.

Azo dyestuffs containing hydroxy groups in which the hydroxy group occupies the *para* position to the azo group are sensitive to alkalies, by which they are changed from yellow to orange, or from red to maroon. This sensitiveness to alkalies is removed if the hydrogen of the hydroxyl groups is replaced by an alkyl group (methyl or ethyl). Thus the dyestuff Brilliant Yellow, which has the constitution



$$\begin{array}{l} CH.C_6H_3(SO_3H).N_2.C_6H_4.OH \\ \| \\ CH.C_6H_3(SO_3H).N_2.C_6H_4.OH, \end{array}$$

is changed to orange by caustic soda, but upon ethylation is converted into the alkali-fast dyestuff Chrysophenine,



$$\begin{array}{l} CH.C_6H_3(SO_3H).N_2.C_6H_4.OC_2H_5 \\ \| \\ CH.C_6H_3(SO_3H).N_2.C_6H_4.OC_2H_5. \end{array}$$

Hydroxy azo dyestuffs in which the hydroxy group occupies the *ortho* position to the azo group are, however, unaffected by aqueous alkalies, and this constitution is therefore to be preferred, and is mainly employed.

Azo dyestuffs which do not contain a salt-forming group, either acid or basic, are insoluble in water, and in the ready prepared condition are only used as pigment colours (paper staining, printing, etc.), and for colouring oils, waxes, and varnishes. They find, however, a large employment in dyeing and calico-printing when produced upon the fibre itself (cotton) by applying successively an alkaline phenol solution (usually β-naphthol) and a solution of a diazo compound. This method is used, for example, in the production of Para Red (from β-naphthol and diazotised paranitraniline) and of Dianisidine Blue (from β-naphthol and diazotised dianisidine). Azo dyestuffs of this class have neutral properties, and differ from the water soluble azo dyestuffs in being soluble in organic solvents. They are therefore removed from the fibre upon extraction with pyridine, chloroform, etc. They are also more or less volatile under heat, a fact which can be made use of to distinguish, for instance, Para Red from Turkey Red, the colour of the former disappearing when the fibre is heated over a small flame.

The azo dyestuffs may be conveniently subdivided on the basis of their dyeing properties into the following divisions:

(*a*) *Basic Azo Colours.*—A small group represented by Bismarck Brown, Chrysoidine, Tannin Orange, and by the Safranine-azo colours (Janus Blue, etc.).

(*b*) *Acid Azo Colours.*—A large group to which the ordinary wool yellows, oranges, scarlets, blacks, etc., belong.

(*c*) *Mordant Azo Colours.*—A group consisting of "acid mordant" or "chrome" colours, chiefly used for dyeing wool in shades fast to milling.

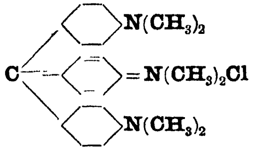
(*d*) *Direct or Salt Azo Colours.* — Employed chiefly in the dyeing of cotton and linen.

(*e*) *Neutral or Pigment Azo Colours.*—Comprises Oil Yellow, Sudans, Para Red, Dianisidine Blue, etc., and some of the colouring-matters employed as pigments, such as Pigment Orange R, Helio Fast Red RL, Pigment Purple, etc.

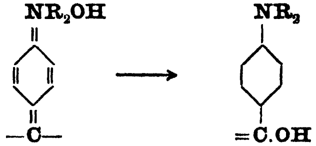
IV. Triphenylmethane Class.—*Typical groupings:*

and

The dyestuffs of this class have mostly a very brilliant shade, red, violet, blue, or green. Its members, of which Methyl Violet,



may be taken as a typical representative, may have "basic," "acid," or "mordant" dyeing properties. As a class the triphenylmethane dyestuffs, more especially those having basic properties, are rather deficient in fastness to light. Many of them, such as the Alkali Blues, Acid Greens, etc., are very sensitive to the action of alkalies or soap, by which they are decolourised. This loss of colour is to be attributed to a conversion of the quinonoid compound into a colourless benzenoid carbinol according to the general equation:



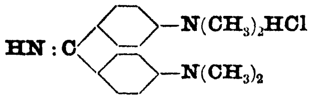
The tendency for this change to occur, which is present in varying degree throughout the entire class, is greatly diminished by the introduction of a sulphonic or halogen group in an *ortho* position to the methane carbon. The dyestuffs of the Patent Blue series and some of the Acid Violets possess such an ortho-sulphonic group, and exhibit in consequence superior fastness to washing and milling. A similar effect is obtained in the "basic" members (Setoglaucines and Setocyanines) by the introduction of an ortho-situated chlorine atom.

The "basic" members of the triphenylmethane class are represented by Fuchsine, Methyl Violet, Malachite Green, Brilliant Green, Setoglaucine, Setocyanine, Victoria Blues, etc.

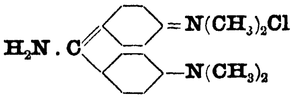
The "acid" members comprise Acid Fuchsine, Soluble and Alkali Blues, Wool Blues, Acid Violets, Acid Greens, Patent Blues, Ketone Blues, etc. Certain of these (sulphonic acids of betanaphthylated rosanilines) exhibit a certain degree of "direct" affinity for cotton, upon which they give bright greenish-blue shades when used alone or in admixture with azo salt dyes (Titan Como, Chlorazol Brilliant Blue, Isamine Blue, etc.).

The "mordant-dyeing" members of the triphenylmethane class are represented by Chrome Violet, Chrome Green, Eriochrome Cyanine, Eriochrome Azurol, and the Chromoxane colours.

Closely related to the triphenylmethane colouring-matters is the yellow "basic" dyestuff Auramine, which may be regarded as a derivative of diphenylmethane. It has the structure:

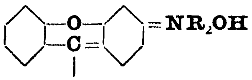


or

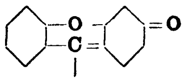


This dyestuff is readily decomposed upon boiling with acids giving an ammonium salt and the colourless tetramethyl-diamidobenzophenone. It also exhibits the peculiar property of producing an unstable violet colouration upon reduction with zinc dust and an acid, due to the formation of a quinonoid salt of tetramethyldiamidodiphenylcarbinol.

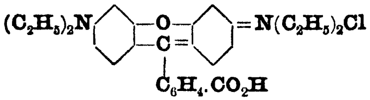
V. Pyrone or Phthalein Class.—*Typical groupings:*



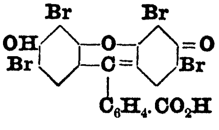
and



This class, consisting partly of "acid" and partly of "basic" members, comprises some of the most brilliant dyestuffs known. They are less liable than the triphenylmethane colours to undergo conversion into colourless carbinol forms, and are hence faster than the former to alkalies, soap, and milling. The Rhodamines are "basic" members of the class, represented by the first of the above general formulæ. Thus Rhodamine B has the constitution:



The Eosines are the corresponding phenolic analogues containing the typical grouping shown by the second general formula above. Thus Eosine A has the constitution:

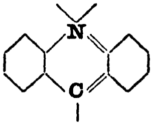


The Acid Eosines, Acid Rhodamines, and Violamines or Fast Acid Violets contain in addition to the basic or phenolic groups, also sulphonic groups (SO_3H). The Eosines are capable of yielding unstable metallic compounds, and in the form of their lead salts are employed for the preparation of red pigment colours ("Vermilionettes"). More definite "mordant-dyeing" properties are possessed by Gallein and the Chromorhodines, the former of which is used in calico-printing under the name of Alizarine Violet.

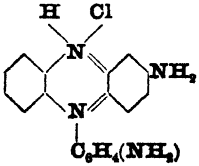
In their behaviour towards reducing agents the pyrone colours are distinguished from the triphenylmethane dyestuffs by greater resistance to decolourisation, and when reduced give leuco compounds which are rather more oxidisable by air. In this latter respect they occupy a somewhat intermediate position between the para- and the ortho-quinonoid dyestuffs. The violet and blue members of the class, such as Fast Acid Blue, approach the ortho-quinonoid dyestuffs in the facility with which their leuco compounds are oxidised.

The Eosines, when not containing a sulphonic group, are readily taken up from *acid* media by ether, giving yellow solutions which become pink on evaporation of the solvent and addition of an alkali. On the other hand the unsulphonated Rhodamines, being "basic," are taken up by ether from a *neutral* or *alkaline* solution. The sulphonated members of both classes are entirely insoluble in ether. The Eosines, being brominated or iodated compounds, are further characterised by the evolution of the respective halogen when heated with concentrated sulphuric acid and oxide of manganese. Most of the members of the pyrone class exhibit in solution a more or less pronounced fluorescence.

VI. Acridine Class.—*Typical grouping:*



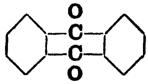
This is a small class of yellow and orange dyestuffs, containing "basic" members only. They find their chief employment in calico-printing and leather dyeing. The typical representative of the class is Phosphine,



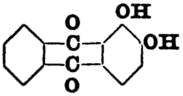
Other members are Acridine Yellow, Acridine Orange, Benzoflavine, Rheonine, Coriphosphine, Euchrysine, Aurophosphines, etc.

The acridine dyestuffs are somewhat resistant to reduction, and are therefore not decolourised on the animal fibre by hydrosulphite. They mostly exhibit a marked green fluorescence, when dissolved in concentrated sulphuric acid or alcohol.

VII. Anthracene or Anthraquinone Class.—*Typical grouping:*



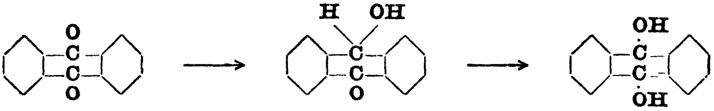
This important class contains "acid," "mordant," and "vat-dyeing" members, all of which are remarkable for great fastness to light. The older members of the class, comprising Alizarines, Purpurines, Alizarine Orange, Alizarine Blue, Alizarine Cyanines, Anthracene Blues, etc., are "mordant" colouring-matters dyeing upon aluminium, chromium, or iron. With these mordants very fast colours are produced, the shades of which vary with the mordant employed. Thus the typical dyestuff of this class, Alizarine,



yields with aluminium a red, with chromium a maroon, and with iron a purple. When fixed upon a compound mordant of aluminium, calcium, and a fatty acid, it produces the celebrated Turkey Red. The "acid" members of the class are represented by the Alizarine Reds (WS, etc.), Alizarine Acid Blue, certain marks of the Alizarine Cyanines and of the Anthracene Blues, Acid Alizarine Green, Alizarine Saphirol, Alizarine Astrol, Alizarine Irisol, Alizarine Cyanol, Alizarine Direct Blue, Violet, and Green, Cyananthrol, Alizarine Cyanine Green, Alizarine Viridine, Anthraquinone Blue, Violet, and Green, etc. Whilst many of these belong to the class of "acid-mordant" dyestuffs, others again are true "acid" colours requiring no mordant for their fixation (Alizarine Saphirol series, Alizarine Direct colours, etc.).

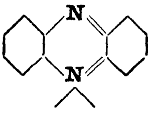
The "vat" dyestuffs of the anthraquinone class, the first of which was discovered in 1901, are now a numerous and important division (Indanthrene series, Algol series, Cibanone colours). In their extreme resistance to light and other agencies they constitute the fastest dyestuffs known. Many of these compounds have a very complex structure containing two or more anthraquinone residues. For the most part they do not sublime when heated, and are thus distinguished from the "vat" dyestuffs of the indigoid class. Two or three of the simpler members, however, form an exception to this rule.

All the anthraquinone dyestuffs, whether belonging to the "mordant," "acid," or "vat" classes, exhibit the peculiarity, already mentioned, of giving *coloured* leuco compounds. This is to be referred to the reduction of one CO group to a $-CH(OH)$ group, leaving the second CO group to assume a quinonoid form:



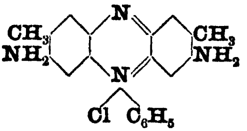
The leuco compounds are in many cases reoxidised to the original dyestuff by air alone, but in other cases a stronger oxidising agent is required. Their colour often differs remarkably from that of the original dyestuff: for example, the leuco compound of the yellow Flavanthrene is blue, reoxidising in air to yellow. The application of stronger reducing agents frequently converts the first leuco compound into a more stable second leuco compound from which the dyestuff is difficult to regenerate.

VIII. Azine Class.—*Typical grouping:*



This class contains both "basic" and "acid" dyestuffs which range in shade from red through violet to blue. Whilst the "basic" members of the class are mainly represented by the Safranines, Rhodulines, and Spirit Indulines, the "acid" members comprise the Rosindulines, Soluble Indulines, Nigrosines, and the recently introduced Wool Fast Blue and Wool Fast Violet.

The typical representative is Safranine:



whilst Perkin's Mauve, the earliest coal-tar dyestuff, belongs to this group. Certain "basic" members which are insoluble in water

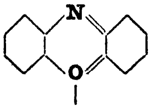
(Indulines and Nigrosines) are employed in the form of their salts with oleic, linoleic, or stearic acids to colour oils and waxes (for boot polishes, lacquers, printing inks, etc.).

As already mentioned under Class III., "basic" dyestuffs containing both the azine and the azo chromophor, obtained by coupling diazotised Safranines with naphthols, etc., are employed under the names of Indoin Blue, Janus Blue, Janus Green, etc., chiefly in calico-printing. They exhibit upon reduction a characteristic behaviour, the azo residue being split off and the leuco compound of the parent Safranine formed, which upon exposure to air becomes red, or if formaldehyde is present (reduction with hydrosulphite formaldehyde compounds) violet.

Many red and violet dyestuffs of the azine class exhibit the property of dissolving in concentrated sulphuric acid to a green solution, which on dilution with water passes through blue to the original shade.

Aniline Black is a black insoluble dyestuff which is produced on the cotton fibre by oxidation of salts of aniline with chlorates or bichromates. It has been shown recently[1] that this dyestuff is a very complex azine. It is insoluble in all solvents and cannot therefore be extracted from the fibre. Like other azines it is reduced to a leuco compound which is very rapidly reoxidised by air. The estimation of Aniline Black on the cotton fibre can be effected, after removing all finishing materials and other dyestuffs, by determining the nitrogen present by the Kjeldahl method, using about 5 grams of cloth for each estimation. The percentage of nitrogen found, subtracting 0·1 per cent. for that normally present in the cotton fibre, gives when multiplied by the factor 6·6 the percentage of Aniline Black. The Aniline Black can also be separated from the fibre by dissolving the cotton in cold concentrated sulphuric acid and, as soon as solution is complete, pouring into cold water, when the dyestuff is thrown down as a greenish-black voluminous precipitate which is filtered off, washed with water, and dried.

IX. Oxazine Class.—*Typical grouping:*



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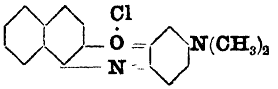
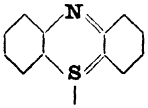
[1] A. G. Green and collaborators, *J. Soc. Dyers and Cols.*, 1913, pp. 105 and 338.

This class is chiefly represented by blue "basic" and "mordant" dyestuffs, of which Meldola's Blue,

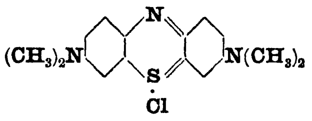


may be taken as a typical example. This, together with Nile Blue, Capri Blue, and Cresyl Blue, are "basic" dyestuffs; whilst the Gallocyanines, Prune, Gallamine Blue, Celestine Blue, Delphine Blues, Phenocyanines, Modern Violet, Gallo Violet, Modern Cyanines, Chrome Azurines, Anthracyanine, Ultraviridine, Gallo Green, etc., are "mordant" dyestuffs largely used in calico-printing. Most of these latter possess "basic" as well as "mordant" dyeing properties, and hence form lakes both with tannin and with chromium salts. They may therefore be termed "basic-mordant" colours.

X. Thiazine Class.—*Typical grouping:*

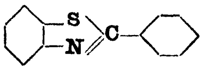


This class, also mainly represented by blue dyestuffs, includes members of the "basic," "acid," and "mordant" divisions. Its most important representative is Methylene Blue,

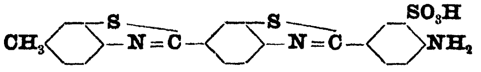


Azocarmine is an "acid" member of the class, whilst Indochromine, Brilliant Alizarine Blue, and Gallothionine Violet are "mordant" dyeing members. The thiazine chromophor is probably also present in the blue and black dyestuffs of the "sulphide" class.

XI. Thiazol or Thiobenzenyl Class.—*Typical grouping:*



The most important member of this class is the diazotisable dyestuff, Primuline,[1] in which the typical thiazol group is repeated twice,



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[1] A. G. Green, *J. Soc. Chem. Ind.*, 1888, **7**, 179; *J. Chem. Soc.*, 1889, **55**, 227.

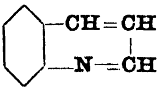
This dyestuff dyes cotton directly in primrose-yellow shades, which when diazotised and coupled with phenols on the fibre can be converted into various other colours (yellow, orange, red, maroon, etc.) remarkable for their excellent fastness to washing. Thus, the most used Primuline Red is produced by passing cotton dyed with Primuline through a solution of nitrous acid (sodium nitrite acidified with hydrochloric acid) and then through an alkaline bath of betanaphthol, when the red is at once developed.

Certain other members of the thiazol class (Chloramine Yellow, Chlorophenine, Thiazol Yellow, Thioflavine S, etc.) also possess a direct affinity for cotton, *i.e.* are "salt" dyestuffs, but as they do not contain an amido group, they are not diazotisable. The dyestuff Thioflavine T has "basic" properties, and is used in calico-printing for the production of pure greenish-yellow shades with a tannin mordant.

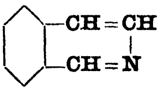
Some members of the class contain an azo group in addition to the thiazol grouping (*e.g.* Dianil Yellow, Erica, Diamine Rose, Geranine, etc.). These also have a direct affinity for cotton.

The thiazol chromophor is difficult to reduce, and those dyestuffs containing this group alone are but little affected by reducing agents or only become rather paler. When, however, as is the case with the developed colours from Primuline, an azo group is also present, the latter suffers disruption and the yellow parent thiazol compound remains.

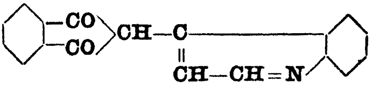
XII. Quinoline and Isoquinoline Class.—*Typical groupings:*



and



This class is a small one, comprising only one member used in dyeing, viz. the fast greenish-yellow dyestuff Quinoline Yellow, which has the constitution:

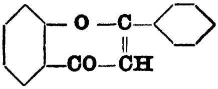


The compound itself is insoluble in water and is therefore only used for colouring varnishes and oils, but its disulphonic acid, Quinoline Yellow O, is a valuable "acid" dyestuff for wool and silk, giving shades fast to light.

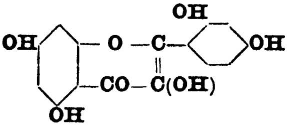
Other members of the quinoline class are for the most part very fugitive to light, and although unsuitable as dyestuffs for fibres, find application as photographic sensitisers and in colour photography (Cyanines, Quinoline Red, Ethyl Red, Orthochrome Colours, etc.).

The dyestuffs of the quinoline series, like those of the thiazol class, are resistant to reduction and therefore difficult to decolourise.

XIII. Flavone Class.—*Typical grouping:*

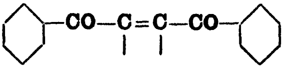


The representatives of this class at present in use are all natural dyestuffs and mostly possess "mordant" dyeing properties. They comprise the colouring principles of Fustic, Weld, Quercitron, Persian Berries, etc.; thus morin, the colouring-matter of Fustic wood, has the constitution:

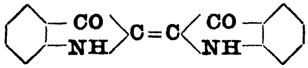


The colouring-matters of other dye-woods, such as those of Logwood (hæmatein), Brazilwood (brazilein), Cutch (catechin), also contain closely related chromophoric groups. The dyeing principles generally exist in the fresh dye-woods in the form of glucosides or leuco compounds. From these substances the dyestuffs proper are formed during extraction or use. Their compounds with mordants are somewhat easily decomposed by acids, so that they are stripped from the fibre even by dilute acid solutions, more particularly when dyed upon aluminium or iron. With mineral acids, Logwood (hæmatein) gives a characteristic bluish-red solution, which serves to identify this dyestuff or to separate it from mixtures.

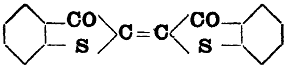
XIV. Indigoid Class.—*Typical grouping:*



This class, which until a few years ago was only represented by Indigo itself and its sulphonic acids (Indigo Carmine), has been recently greatly extended. It now contains dyestuffs of almost every shade (Thioindigo series, Helindone series, Ciba series, etc.). With the exception of the "acid" dyeing and fugitive Indigo Carmine, these dyestuffs all belong to the class of "vat" colours and are remarkable for great fastness to light and other influences. The typical representatives are Indigo Blue



and Thioindigo Red,



Many members of the class contain chlorine or bromine atoms in substitution for hydrogen in the nucleus; thus Ciba Blue 2B is a tetrabromo derivative of Indigo.

The indigoid "vat" dyestuffs are insoluble in water, but become soluble upon treatment with alkaline reducing agents by formation of alkali salts of the leuco compounds. These leuco compounds are of a pale yellow colour and are readily reoxidised by air. The dyestuffs are volatile at a high temperature, giving coloured vapours of a similar tint. Being more or less neutral in properties they can be extracted from the animal or vegetable fibre by organic solvents such as pyridine, glacial acetic acid, cresol, aniline, and (to a less extent) chloroform. The solubility in pyridine, acetic acid, and cresol has been used as a means of separating Indigo from accompanying dyestuffs in the analysis of mixed shades on wool.

As already mentioned, a large number of the indigoid dyestuffs contain halogen atoms in the nucleus, more especially bromine (Ciba Blue, Bromindigo, Indigo MLB/4B, 5B, 6B, Brilliant Indigo, Ciba Violet, Ciba Heliotrope, Thioindigo Scarlet G, etc.). In such dyestuffs the presence of the halogen can be detected by heating with oxide of manganese and concentrated sulphuric acid.

Indigo itself, which still remains the premier blue dyestuff, though formerly obtained entirely from the indigo plant (various species of the genus *Indigofera*) is now manufactured in great measure synthetically, the starting-point being the hydrocarbons benzene or naphthalene. It is stated that the world's consumption of synthetic Indigo is at present 7000 tons of 100 per cent. dyestuff per annum. On account of the great importance of Indigo in cotton and wool dyeing a large amount of attention has been devoted to its analysis, and this subject will therefore be considered in a special chapter.

CHAPTER III.

CLASSIFICATION OF DYESTUFFS (*continued*).

B. DYEING CLASSES.

IN the foregoing pages the organic dyestuffs have been considered from the point of view of their chemical structure, that is, in relation to the chromophors they contain. If, however, we employ as the basis of classification the respective affinities and methods of application to animal and vegetable fibres, the dyestuffs may be classed into the following divisions, in each of which will be found members belonging to more than one chemical class.

I. Basic Dyestuffs.—These are salts, usually hydrochlorides, but sometimes sulphates or oxalates, of dye-bases. They owe their basic properties to the presence in the nucleus of amido, alkylamido, or ammonium groups, such as $-NH_2$, $-(NCH_3)_2$, $-N(C_2H_5)_2$, $-NHC_6H_5$, $-N(CH_3)_3OH$, etc. They dye animal fibres directly from a neutral bath, but possess for vegetable fibres (jute excepted) only a small affinity. They are therefore applied to the latter fibres by previously mordanting the material with tannate of antimony, or sometimes with tannates of tin, aluminium, or iron. This is effected by steeping in a tannin bath, followed by passage through a solution of a metallic salt such as antimony potassium tartrate. In calico-printing, for which dyestuffs of the " basic " class find their chief application, a thickened mixture of the dyestuff with tannin and acetic acid is printed upon the cloth, which is then steamed. This drives off the volatile acid, leaving the dyestuff tannate, which is then converted into the insoluble double tannate of dye-base and antimony by passage through a solution of an antimony salt. Other classes of dyestuffs, such as the "salt," "mordant," or "sulphide" colours, can, when dyed upon cotton, serve as mordants for "basic" dyestuffs. This fact is frequently made use of in "topping" colours obtained with the former classes in order to increase their brilliancy of shade. A similar procedure is sometimes followed in dyeing silk, an "acid" dyestuff being applied first and a "basic" dyestuff afterwards. The "basic" dyestuffs can be applied to jute without a mordant and are used extensively for dyeing this material. In leather dyeing they are also employed. Salts of the dye-bases with the higher fatty acids, such as the oleates, linoleates, stearates, resinates, etc., are insoluble in water but dissolve in hydrocarbon solvents. They are used for colouring oils, candles, varnishes, etc., and in so-called "dry dyeing." The "basic" dyestuffs are also employed in the manufacture of lake pigments for wall-paper printing, etc., for which purpose they are usually precipitated as double tannates or phosphates upon a mineral substratum. They also find employment in the colouring of a large variety of other articles, as, for example, confectionery, artificial flowers, etc.

The addition of caustic soda to a solution of a "basic" dyestuff usually precipitates the dye-base, but in some cases (*e.g.* Safranine) no precipitation occurs. All the "basic" dyestuffs readily form insoluble tannates. The production of a precipitate upon the addition of a solution of tannin and sodium acetate therefore constitutes the best test for distinguishing the "basic" colours from the members of other dyeing groups.

The "basic" dyestuffs owe their affinity for the animal fibres to the amido or alkylamido groups they contain, which probably enter into chemical combination (salt formation) with the carboxy ($-CO_2H$) groups of the wool or silk proteins. They exert their maximum affinity for these fibres in a neutral or slightly alkaline bath, and conversely the dyestuff is partly stripped again if the dyed fibre is boiled with a dilute acid. Loss of colour upon boiling with a 5 per cent. solution of acetic acid therefore forms a suitable test for distinguishing dyestuffs of this class when fixed upon animal fibres. Upon vegetable fibres (cotton or linen) it is necessary before this test can be applied to remove the tannin mordant, which can be conveniently effected by boiling with dilute caustic soda saturated with common salt.

II. Acid Dyestuffs.—These are salts, usually sodium salts, of colour-acids. They owe their acid properties to the presence in the nucleus of sulphonic groups ($-SO_3H$), carboxylic groups ($-CO_2H$), or nitronic groups ($=NO_2H$). The large majority of such colour-acids contain the sulphonic group.

The acid dyestuffs only give precipitates with mineral acids in exceptional cases; usually the free colour-acid is easily soluble in water, and therefore remains dissolved. The "acid" dyestuffs give no precipitates with tannin and sodium acetate, although certain of them which contain amido or alkylamido groups in addition to sulphonic groups (as, for example, Acid Violets, Acid Greens, etc.) exhibit some "residual basic" properties, so that when the sulphonic group is sufficiently weighted, as, for instance, by combination with barium, a precipitation with tannin may occur. This fact is sometimes utilised in the production of lake-pigments from dyestuffs of this class.

The "acid" dyestuffs dye wool and silk directly from an acidified solution. Certain of them, notably Acid Violets, Wool Blues, Quinoline Yellow, etc., will also dye wool to some extent from a neutral bath, a property which is made use of in the "single-bath" method of "union" dyeing. For cotton and other vegetable fibres they have little or no affinity. They find their chief application in the dyeing and printing of wool and silk, but are also employed to some extent for colouring cotton and jute when these materials are not required to be washed (bookbinding cloths, jute rugs, etc.).

In the production of lake-pigments many of the "acid" dyestuffs are extensively employed (*e.g.* Azo Scarlets, Azo Oranges, Eosines, etc.), for which purpose they are precipitated upon a mineral substratum by addition of barium chloride or lead acetate. Some of the newer dyestuffs of this class, which are specially manufactured for lake-making, are Lithol Reds, Pigment Scarlets, Lake Bordeaux, Radial Yellows, Pigment Fast Yellows, etc.

The "acid" dyestuffs owe their affinity for animal fibres to the sulphonic or other acid groups which they contain, and which doubtless enter into chemical combination (salt formation) with the "basic" groups of the wool or silk. For this reason the dyestuffs of this class are very deficient in fastness to alkalies and soap, which by neutralising the colour-acid loosen its attachment to the fibre. Loss of colour upon boiling the dyed material with 1 per cent. ammonia solution affords therefore a convenient means for recognising dyestuffs of this type. It is to be noted, however, that in addition to the above-mentioned typical "acid" dyestuffs, there exists a considerable number of colouring-matters, which from their method of application might be regarded as belonging to the "acid" class, but which possess a higher resistance to alkalies, and therefore are but little stripped upon boiling with 1 per cent. ammonia. They are frequently termed "fast-acid" dyestuffs, and their greater resistance to alkalies may be referred to their possessing a supplementary attraction for the fibre in addition to that exerted by their acid groups. This may be due to the presence of either (*a*) basic groups, (*b*) mordant-dyeing groups, or (*c*) "direct" dyeing structure.

(*a*) The influence of residual "basic" properties has been already mentioned, and is manifested in the greater affinity for the animal fibre exhibited by certain Acid Violets, Violamine B, Brilliant Milling Blue, etc.

(*b*) Dyestuffs containing hydroxy $(-OH)$ groups in addition to sulphonic or carboxy groups, frequently possess both "acid" and "mordant" dyeing properties. They are termed "*acid-mordant*" or "*chrome*" dyestuffs, and occupy an intermediate position between the ordinary "acid" and the "mordant" colouring-matters. They may be applied to animal fibres either from an acidified bath like ordinary "acid" dyestuffs or by means of a metallic mordant (usually a salt of chromium or copper). In the latter case the dyed fibre exhibits the superior fastness to alkalies, soap, and milling which is characteristic of colouring-matters of the "mordant" class. During recent years the dyestuffs of this category have become of great importance for wool dyeing, as many of them are capable of application by the single-bath method ("metachrome" or "monochrome" process), in which the mordanting and dyeing operations are effected simultaneously by the addition of a chromate to the dye-bath. This principle has been extended even further by supplying to the consumer ready prepared chromium or copper compounds of the respective colouring-matters, which then dye like ordinary "acid" dyestuffs (Mercerol colours, etc.). The detection of the metallic mordant on fibres dyed with these products requires special care on account of the small quantity of the metal present.

(*c*) Another category of "acid" dyeing colours also possessing a high degree of resistance to alkalies and milling are closely allied in chemical composition to the "direct" dyeing cotton dyestuffs (salt colours). These are the Sulphone Cyanines, Sulphone Azurines, Milling Red, etc. They exhibit a certain affinity for cotton, though not so pronounced as that of the more typical "salt" dyestuffs.

III. Salt or Direct Dyestuffs.—These are dyestuffs which dye cotton and other vegetable fibres from a neutral or alkaline solution without the application of a mordant. They dye animal fibres in a similar manner, and also from an acid bath. Like the "acid" dyestuffs they consist of salts, usually sodium salts of sulphonic acids; but whilst in the case of the "acid" dyestuffs it is the free colour-acid which is taken up by the fibre, the "salt" dyestuffs are absorbed as a whole. The cause of this "direct" affinity is not at present known, though it appears to be associated with a certain symmetry of molecular structure, and may be due to an attraction between the hydroxyl groups of the fibres and the azo or other chromophor of the dyestuff. It is noteworthy that the affinity of the "salt" dyestuffs for cotton is entirely lost when the hydroxyl groups of the latter are etherified.

The "salt" dyestuffs are mainly used in cotton dyeing and printing; also in dyeing "unions" (mixtures of cotton and wool). Certain of them (such as Bordeaux Extra, Fast Diamine Red, Cloth Brown, Sulphone Azurines, Sulphone Cyanines, etc.) are employed in wool dyeing, giving on this material colours of superior resistance to washing and milling. Whether dyed upon vegetable or animal fibres, the "salt" dyestuffs always exhibit a certain tendency to stain white cotton when the latter is boiled with the dyed material in a weakly alkaline solution. This tendency, which may be employed as a test for dyestuffs of this class, is, however, greatly diminished by "after-treatment" of the dyed material.

A few of the "salt" dyestuffs contain "mordant-dyeing" *i.e.* hydroxyl groups (*e.g.* Anthracene Red, Salicine Yellow, etc.) and may be termed therefore "*salt-mordant*" colours. They are employed in wool dyeing with a chrome mordant.

The "salt" dyestuffs can be subdivided according to their chemical structure into the following categories:

(1) *Diamine Colours*, consisting of disazo and trisazo compounds derived from para-diamido bases (benzidine, tolidine, dianisidine, phenylenediamine, naphthylene diamine, diamidodiphenylamine, etc.). These colours are completely reduced by zinc-dust, stannous chloride, titanious chloride, or hydrosulphites, to colourless amido compounds. They include amongst others the dyestuffs of the Benzo, Congo, Diamine, Dianil, Oxamine, Columbia and Chlorantine series.

(2) *Thiazol Colours*, some of which (Primuline Yellow, Thiazol

Yellow, Chloramine Yellow, etc.) contain the thiazol group only, whilst others (Erica, Geranine, Diamine Rose, Developed Primuline colours, etc.) also contain an azo group. The former are but little affected by reducing agents, whilst the latter suffer reduction of the azo group, changing thereby from red to yellow.

(3) *Stilbene Colours*, including Curcumine or Direct Yellow, Mikado Yellows and Oranges, Stilbene Yellows, etc. These are azo dyestuffs derived from stilbene or diphenylethylene, $C_6H_5 - CH = CH - C_6H_5$. They are reduced to colourless hydrazo compounds which reoxidise in air to orange, and only upon long boiling with reducing agents are permanently decolourised. They exhibit a greater degree of fastness both to washing and light than the colours of the diamine class.

(4) *Derivatives of J-Acid.*—These are mono and disazo dyestuffs obtained by coupling diazo compounds with derivatives of the so-called J-acid (amidonaphthol sulphonic acid 2 : 5 : 7). They comprise the Rosanthrenes, Benzo Fast Scarlets, Diazo Brilliant Scarlets, Diamine Azo Scarlets, Dianil Scarlets, Zambesi Reds, Dianol Fast Red and Blue, Azidine Scarlets, etc. The reds are distinguished from those of the diamine series (Benzopurpurines, etc.) by being unaffected by acids. Upon reduction they are completely broken up and decolourised.

(5) *Azoxyamine Colours.*—These are disazo derivatives of metadiamidoazoxy compounds. They differ from the other members of the "salt" class in requiring to be applied to cotton from a caustic alkaline bath. They comprise the dyestuffs, St Denis Red or Rosophenine and Milling Scarlet. Upon cotton they are tolerably fast to washing and are not changed in shade by acids.

In addition to the above classes, two natural dyestuffs, namely, the colouring principles of Turmeric and Annatto, dye cotton without a mordant. Also, as already mentioned, the sulphonic acids of betanaphthylated rosanilines (Titan Como, Brilliant Chlorazol Blues, Isamine Blue, etc.), have a certain degree of "direct" affinity for cotton. Some brands of these latter are mixtures with "salt" dyestuffs of the azo class.

As already mentioned, the fastness of the "salt" colours to washing, and in some cases to light, is greatly increased by an "after-treatment" or chemical modification of the colouring-matter upon the fibre. Four different methods of "after-treatment" are in use, viz.:—(*a*) Boiling in a solution of a chromium or copper salt or of a mixture of the two. (*b*) Steeping in a dilute solution of formaldehyde. (*c*) Diazotising and developing with a phenol. (*d*) Coupling with diazotised paranitraniline.

The first method is applicable to a large number of diamine colours, especially the blues, browns, and blacks, which are converted thereby into their chromium or copper salts. The second is especially adapted to dyestuffs containing in their molecules resorcin or phenylenediamine residues (Vulcan Black, Benzoform colours, etc.), the formaldehyde presumably effecting the union of two molecules by introduction of a methylene (CH_2) group. The application of the third and fourth methods will be considered under the heading "Developed Colours" (Class VI.).

IV. Mordant Dyestuffs.—The "mordant" dyestuffs are a large and important class of products, partly of natural and partly of artificial origin, which are characterised by forming stable coloured lakes with metallic hydroxides. They owe this property to the presence in the molecule of one or more hydroxyl ($-OH$) groups. These groups usually occupy by preference an ortho position to the chromophor (*i.e.* to the azo, oxazine, thiazine, ketonic, or nitroso group of the dyestuff); or in some cases the hydroxyl group is para to the latter whilst ortho to a carboxylic ($-COOH$) group. To the category of "mordant" dyestuffs belong most of the older natural colouring-matters, such as those derived from Fustic, Persian Berries, Logwood, Brazilwood, Cochineal, Cutch, etc. It also includes many of the fastest artificial dyestuffs.

The various members of the group differ greatly in properties. Some, such as alizarine and hæmatein (Logwood), have, when used alone, but little colouring power, and only develop their colour in combination with metallic mordants. Others, for example gallein, are strongly coloured, but when applied without a mordant have but little affinity for the fibre. Others again contain sulphonic or carboxylic acid groups in addition to hydroxy groups. They dye animal fibres like the ordinary "acid" dyestuffs, but evince a much greater degree of fastness to washing, milling, and light when applied with a mordant; they are termed "*acid-mordant*" colours, "*chrome*" colours, or "*acid alizarines.*" In many cases combination with a mordant brings about a complete change of shade, which may depend on the metal introduced. Thus alizarine gives a red with aluminium and a purple with an iron mordant; hæmatein gives a blue with aluminium and a bluish-black with chromium; the red Chromotropes are changed to dark blue or black by chromium salts or chromates; and with the same mordant the red Eriochrome Azurol becomes blue.

Whilst formerly the salts of aluminium, iron, and tin were frequently employed as mordants, most of the modern dyestuffs of the "mordant" and "acid-mordant" class are fixed by means of chromium. This metal, besides giving the fastest lakes, has the advantage of being easily applied in the form of chromate or bichromate. In connection with the employment of the "acid-mordant" colours in wool dyeing, the "single-bath" method of application has recently gained greatly in importance, the dyeing taking place in a bath containing a chromate or bichromate (Metachrome colours, Monochrome colours, Orthochrome colours, etc.). In other cases the wool is mordanted either before or after dyeing (see also under "acid" dyestuffs).

Another category of "mordant" dyestuffs are those containing alkylamido groups ($-NR_2$) in addition to the hydroxy groups. These are chiefly employed in calico-printing for producing fast violet to blue shades with a chrome mordant, and may be termed "*basic-mordant*" colours (for example the Gallocyanines). They are distinguished by giving precipitates with tannin and sodium acetate, as well as with chromium fluoride.

Still another category of "mordant" dyestuffs are related chemically to the "salt" dyestuffs and hence have a "direct" affinity for cotton and other fibres. For this reason white cotton is slightly stained when boiled with the dyed material in a 5 per cent. solution of sodium acetate. They may be termed "*salt-mordant*" colours, and are mainly employed for dying wool (Anthracene Red, Salicine Yellow, Chrome Fast Red, Salicine Red, etc.).

The most important of the plain "mordant" colours (containing no other dyeing group) are alizarine, hæmatein, and Cutch. The first is largely used for dyeing the important Turkey Red upon cotton, a complex lake in which alizarine is combined with aluminium and calcium and also with a fatty acid. Logwood is now but little used for cotton, though still largely employed in dyeing blacks upon wool, and as a "topping" colour for Indigo (chromium, or copper and iron mordant). Cutch is employed for dyeing a fast brown upon cotton by oxidation with a bichromate and copper sulphate. The other natural dyestuffs having "mordant" dyeing properties, though formerly of considerable importance (Barwood, Brazilwood, Cochineal, etc.), have now been largely replaced by artificial dyestuffs, which are cheaper and generally faster.

The various classes of "mordant" colours, especially when fixed upon chromium, exhibit great fastness to alkalies and hence to washing and milling, whilst their resistance to light, more particularly in the case of those belonging to the anthraquinone group, is usually good.

The only general method available for distinguishing "mordant" dyestuffs on the fibre from other alkali-fast colours consists in seeking the metallic hydroxide. In drawing conclusions, however, care must be taken to exclude other possible sources of metallic compounds: such as zinc or calcium chloride introduced in "finishing"; chromium from bichromates used in "stripping" shoddy wool; copper or chromium employed for fixing "salt" colours; bichromates and copper salts employed in the production of oxidation colours; etc.

The "mordant" dyestuffs are for the most part not stripped from the wool or cotton fibre by boiling pyridine, which may therefore be used as a means of differentiation or separation from those "vat" dyestuffs and insoluble azo compounds which dissolve in this solvent.

V. Pigment Colours.—Under this heading are classed colours which are not obtained by dyeing with ready prepared dyestuffs, but are produced upon the fibre (or upon mineral substrata) by chemical synthesis. The affinity between the colour and the fibre is not to be attributed to chemical attractions, but is mainly due to the insoluble state of the coloured compound. The dyestuffs are therefore not stripped from the fibre upon boiling with dilute acids or alkalies, and are usually very fast to light. The colouring-matters of this category may be subdivided as follows:

(1) *Oxidation Colours.*—The most important of these is Aniline Black, produced within the cotton fibre by oxidation of salts of aniline by means of chlorates or bichromates in the presence of an oxygen carrier, *e.g.* a salt of copper, iron, or vanadium. These metals remain in part upon the fibre and hence are found in the ash. From the composition of the latter, conclusions may be drawn as to the dyeing process that has been employed. Thus the ash from "Prussiate" Aniline Black will contain much iron and a little

chromium, but no copper; that from an "aged" or "copper" Black much chromium and copper, but no iron; and that from a "single-bath" Aniline Black much chromium, but usually no copper or iron. Aniline Black is largely employed both in cotton dyeing and calico-printing. Other colours belonging to this class are Paramine Brown, Fuscamine, Ursols, Furols, etc. These are produced on the fibre by oxidation of diamines or amidophenols, and are employed in calico-printing and in fur dyeing.

(2) *Insoluble Azo Colours.*—The most important of these are those produced upon cotton by padding the fibre with an alkaline solution of β-naphthol, $C_{10}H_7OH$, drying and passing the material through a solution of a diazo compound, such as diazotised paranitraniline, α-naphthylamine, dianisidine, etc.; or by printing upon the naphthol-prepared cloth a thickened solution of these diazo compounds. Para Red, Naphthylamine Bordeaux, Dianisidine Blue, Chloranisidine Pink, etc., which are produced in this way, are of considerable importance in calico-printing, in which they constitute a distinct style. There has also been recently introduced a series of colours of remarkable brilliancy and fastness, in which the place of the β-naphthol is taken by β-oxynaphthoic anilide,

termed commercially "Naphthol AC."

The azo colours formed on the fibre are insoluble in water and are not stripped from the fibre by boiling with dilute alkalies or acids. Having neutral properties and no chemical attraction for the fibre, they are removed by hot organic solvents such as pyridine, benzene or chloroform. They can also be volatilised from the fibre at a high temperature. The same remarks apply when these colours are employed in the production of pigments (Para Red, etc.) by precipitation on a mineral substratum.

VI. Developed Colours.—Under this heading are conveniently grouped those colours which are produced upon the fibre by the application of the diazo reaction to colouring-matters already fixed upon it.

In contrast to the colours of the preceding division, which are formed on the fibre by chemical synthesis from colourless components without affinity for it, the "developed dyes" are produced from compounds which are themselves dyestuffs and already in combination with the fibre. A more complex dyestuff is thus built up from a simpler one, and the increase of molecular complexity is accompanied by an enhanced fastness to washing and alkalies, and usually by a considerable deepening of shade. Like the ordinary "salt" colours, developed colours are not removed from the fibre by organic solvents such as pyridine or chloroform. They may be subdivided into two classes:

(1) *Ingrain Colours.*—These are produced by diazotisation of diazotisable "salt" dyestuffs on the fibre, followed by combination with a phenol or diamine. This process was first applied by Green in 1887 to the dyestuff Primuline, and consists in passing the dyed material through a cold acidified bath of sodium nitrite, followed by a cold alkaline solution of a phenol or diamine. It was subsequently extended to a variety of "direct" dyeing azo colouring-matters (Diazo Blacks, Diamine Blacks, Zambesi Blues, Oxamine Blues, Diazo Scarlets, Diaminogens, Rosanthrenes, etc.). In the case of Primuline the treatment effects a great change of colour (from yellow to red when developed with β-naphthol), but in most other cases the shade only becomes deeper or darker, and the chief object of the process is to increase the fastness to washing. For a dyestuff to be capable of this treatment it must contain a diazotisable amido group ($-NH_2$), and the reactions may be represented by the following general equations:

$$(a)\ R'.NH_2+HNO_2=R'.N_2.OH+H_2O.$$

$$(b)\ R'.N_2.OH+R''H.OH=R'.N_2.R''.OH+H_2O.$$

β-Naphthol ($C_{10}H_7.OH$), resorcin ($C_6H_4(OH)_2$), and toluylene diamine ($C_7H_6(NH_2)_2$) are the most frequently used developers. The colours thus produced are, like other azo dyestuffs, converted upon reduction into amido compounds. Those derived from Primuline are reconverted into the latter, and this not being further reducible, remains upon the fibre as a yellow colour which can be identified by its capacity for diazotisation and development. On the other hand, those containing azo groups alone are completely converted into colourless soluble products.

(2) *Coupled Colours.*—These colours are produced by passing the dyed material through a solution of a diazo compound, usually diazotised paranitraniline. This process is applicable to a number of "salt" dyestuffs of the disazo and trisazo class, which contain in their molecules the residues of resorcin or of metadiamines. Such dyestuffs are capable of combining with diazo compounds producing azo compounds of greater complexity, thus intensifying the shades

and rendering the colour faster to washing. The "coupling" process is mainly applied for the production (usually upon raw cotton) of fast browns and blacks. A variety of dyestuffs are applicable for this purpose, amongst which may be named Benzo Nitrol Browns, Toluylene Browns, Diamine Nitrasol colours, Paranil colours, Para colours, etc. Upon treatment with reducing agents, "coupled" colours, like other azo dyestuffs, are completely broken up into colourless amido products.

VII. Sulphide Dyestuffs.—This is a group of dyestuffs of very complex structure which possess the property of dyeing cotton or other vegetable fibres directly from a bath containing sodium sulphide. They are produced by heating various intermediate compounds, mostly of the amidophenol class, with alkaline polysulphides. The dyestuffs in their free state are insoluble in water, but they dissolve in an aqueous solution of sodium sulphide, from which solution vegetable fibres are dyed in shades of remarkable fastness to washing. Although their constitution is not as yet fully ascertained, it is tolerably certain that they owe their dyeing properties, which are akin to those of the "vat" dyestuffs, to the presence in the molecule of a chain of sulphur atoms, R.S.S.R or R.S.S.S.S.R. Such a compound upon reduction in an alkaline medium, *e.g.* with sodium sulphide, yields a soluble salt of the sulphydrate R.S.Na, or R.S.S.Na, which when taken up by the fibre regenerates the original insoluble dyestuff upon air oxidation. These colours occupy, therefore, an intermediate position between the "salt" dyestuffs and the "vat" dyestuffs.

Though possessing in common the above-described dyeing properties, the members do not all contain the same chromophor, but belong to several chemical classes. Thus the black and blue members contain the thiazine grouping; the purple and maroon members, the azine grouping; and the yellow, orange, and brown members, the thiazol grouping. Others, again, are derivatives of anthraquinone and occupy therefore an intermediate position between the sulphide colours and the anthraquinone "vat" colours. The most important commercial "sulphide" dyestuffs are those of the Immedial, Kryogene, Katigene, Thiogene, Thional, Cross-Dye, Sulphur, Pyrogene, Eclipse, and Thioxine series. Of special importance are the black dyestuffs of these series, which have now largely replaced Aniline Black in cotton dyeing. The blue members compete with Indigo, whilst the browns are used for dyeing khaki and cutch shades. Upon animal fibres the sulphide colours have up to the present been little used. This is due to the alkalinity of the dyebath occasioned by the sodium sulphide, to overcome which several attempts have recently been made. The commercial products are sold either as insoluble powders, requiring sodium sulphide for their solution, or in a soluble form already containing sodium sulphide.

The behaviour of the dyed colours upon reduction with hydrosulphites depends upon the chromophor present. Thus whilst the black, blue, and violet members give colourless or pale-coloured leuco compounds, readily reoxidised to the original colour by air, the yellow, orange, and brown members remain for the most part coloured.

The chain of sulphur atoms, to which the sulphide dyestuffs owe their dyeing properties, is somewhat unstable, and under the influence of strong acid reducing agents, such as stannous chloride and hydrochloric acid, a part of the sulphur is split off as hydrogen sulphide, which can be readily detected by lead acetate paper. This constitutes a convenient test for dyestuffs of this class, either in substance or on the vegetable fibre, provided that care is taken to exclude other sources of hydrogen sulphide, such as protein compounds in "finishing" compositions, antichlor on bleached cotton, bisulphites, etc. It should also be noted that certain "salt" dyestuffs may give this reaction to some extent, apparently by reduction of sulphonic groups.

The "sulphide" dyestuffs, probably on account of their high molecular weight, are insoluble in organic solvents, and therefore cannot be removed from the cotton fibre by boiling with pyridine, cresol, or chloroform. They do not sublime from the fibre on heating.

Though tolerably fast to light, the "sulphide" dyestuffs are very easily attacked by hypochlorites, which even in weak solution quickly destroy their colour. This peculiarity may be used in certain cases as a means of differentiation.

The "sulphide" colours are sometimes fixed by an after-treatment with a metallic salt, usually a salt of copper, chromium, or zinc. These metals therefore may be found upon the fibre in small quantities.

Closely allied to the "sulphide" dyestuffs in their chemical composition and manner of production, though not in their application, are the recently discovered Hydrone Blues and Violets, which are derived from carbazol. They differ from the ordinary "sulphide" dyestuffs in being insoluble in sodium sulphide, and are dyed from a sodium hydrosulphite solution. They are accordingly classed as "vat" dyestuffs.

VIII. Vat Dyestuffs.—Under this heading are grouped those dyestuffs which, being in themselves insoluble in water, are applied to the fibre in the form of their soluble leuco compounds, followed by reoxidation by air. Indigo is the typical example of the class and was until recently almost the sole representative. During recent years, however, a large number of new members has been discovered by means of which almost every shade of colour can now be produced. These colours are remarkable for a high degree of fastness, not only towards alkalies, acids, and washing, but also for the most part to light, bleaching, and other agencies. Owing to the insolubility of the dyestuffs in water they are usually sold in the form of pastes.

The property of dyeing "in the vat" may be referred to the capacity of forming leuco compounds of weakly acid properties which possess an attraction for the fibre and are readily reoxidised by air. In the case of the "vat" colours belonging to the indigoid and anthraquinone classes this property is attributable to the presence in the molecule of $\rangle\mathrm{C}:\mathrm{O}$ groups, which by alkaline reducing agents are converted into $\rangle\mathrm{C}\langle^{\mathrm{H}}_{\mathrm{OH}}$ groups or their soluble alkaline salts. In the sulphide "vat" colours it is doubtless due to the presence of sulphide groups which yield sulphydro groups by reduction.

The "vat" dyestuffs may be subdivided according to their chemical structure into the three following categories:

(1) *Indigoid Vat Colours*, comprising Indigo and its halogen derivatives, the Thioindigo series, the Helindone series, and the Ciba series. They are dyed from a neutral or slightly alkaline bath and are applicable to both animal and vegetable fibres. The reduction is usually effected by means of sodium hydrosulphite, though in the case of Indigo other reducing agents are also used (fermentation vat, zinc-dust vat, etc.). The indigoid "vat" colours are characterised by forming on reduction pale yellow leuco compounds which slowly reoxidise to the original colour on exposure to air. The dyestuffs are readily soluble in pyridine and

can be extracted from animal or vegetable fibres by this solvent. Chloroform also dissolves them to some extent. At a high temperature they are volatile, forming coloured vapours; and by careful heating may be even sublimed from the vegetable fibre.

(2) *Anthraquinone Vat Colours,* comprising the Indanthrene and Algol series. They also include dyestuffs (Alizarine Indigos) which possess a structure intermediate between the indigoid and the anthraquinone classes; and, further, certain sulphur derivatives of anthracene or anthraquinone (Indanthrene Olive, Indanthrene Black, Cibanone Yellow, Orange, Brown, and Black). The anthraquinone "vat" dyestuffs are employed in dyeing and printing cotton and linen, but as they require for their reduction a strongly alkaline bath, they cannot be applied to animal fibres (except in one or two cases). Reduction is almost always effected by means of sodium hydrosulphite. The leuco compounds are generally deeply coloured, frequently having a darker colour than the dyestuffs themselves. Certain of the simpler members of the class are soluble in pyridine, whilst others of more complex structure are sparingly soluble or insoluble. The above-mentioned sulphur-containing members are differentiated by evolving hydrogen sulphide when the dyestuff or dyed material is boiled with stannous chloride and concentrated hydrochloric acid. With a few exceptions (Helindone Yellow 3G, Algol Scarlet G, Algol Pink R) the anthraquinone "vat" dyestuffs are not sublimable, and the difference in behaviour in this respect may be employed to distinguish them from those of the preceding class.

(3) *Sulphide Vat Colours.*—This category is at present only represented by the Hydrone Blues and Hydrone Violet, which are derived from carbazol and probably contain the thiazine chromophor. They are closely related to the ordinary "sulphide" colours, from which they differ, however, in being insoluble in sodium sulphide. They are dyed like the preceding "vat" colours from an alkaline bath containing sodium hydrosulphite, but are only applicable to vegetable fibres. They yield on reduction nearly colourless leuco compounds which oxidise readily on exposure to air. They are not sublimable, and, like the ordinary "sulphide" colours and the sulphur derivatives of the anthracene class, they are not extracted from the fibre by pyridine. They also evolve hydrogen sulphide when boiled with stannous chloride and hydrochloric acid.

SUMMARY.

Table I. facing this page gives a general survey of the organic dyestuffs based upon the system of classification adopted in the preceding chapters. The total number of individual dyestuffs now in commerce is very large, and space considerations therefore render it impossible to give more than a few examples of each division.

It will be seen that the dyestuffs at present in use, numerous though they are, by no means represent all possible classes, for very many gaps still remain vacant. It is probable that in course of time many of these blanks will be filled, and doubtless also dyestuffs with new chromophors discovered. It is necessary for this reason that our analytical schemes should be as elastic as possible and capable of modification or extension as need may arise.

Some dyestuffs contain two chromophoric groupings, and thus are capable of being classed in more than one position: for example, Indoin Blue is both an azine and an azo compound; Alizarine Orange is a nitro compound of the anthracene series; Indian Yellow is a nitro-azo compound; Erica and Diamine Rose contain both the azo and the thiazol groups; whilst some of the anthracene "vat" colours contain azine or other groups in addition to the anthracene complex. In a similar manner, there are dyestuffs which can be classed in more than one dyeing division: thus the dyestuffs of the gallocyanine series have both "mordant" and "basic" properties; whilst some dyestuffs of the "salt" class have also "mordant" dyeing functions.

CHAPTER IV.

THE ANALYSIS OF COLOURING-MATTERS IN SUBSTANCE.

WITH the continual progress in the synthetic colour industry and the rapid increase in the number of dyestuffs in use, the existence of reliable methods of analysis is of growing importance. It is, for example, essential for the dyer, calico printer, pigment manufacturer, or other user of dyestuffs, to be able to ascertain whether certain products supplied by one firm are or are not identical with products sold under a different name by another. Mere similarity of shade and correspondence in method of application do not suffice alone to establish equivalency. It is of equal importance to know that the competing articles are chemically identical, or at least that they belong to the same chemical class, for upon the chemical constitution of the dyestuff rests its degree of fastness and other important properties, which determine its suitability for the purpose in view. The neglect to chemically control the dyestuffs used, and hence the frequent substitution of one dyestuff by another of similar shade but of different chemical structure, is the chief cause of irregularity and faults in manufactured articles, and of failures to comply with established standards.

Similar analytical problems are also encountered by the public analyst, who may be called upon to ascertain the identity of a dyestuff used for colouring articles of food, or the chemical constitution of a colouring-matter for Customs purposes.

The daily appearance of new products and the new names which are frequently given to old ones render these problems increasingly difficult. When, for example, the only known blue dyestuffs were Indigo, Aniline Blue, and Methylene Blue, it was a simple enough procedure to decide the identity of a given dyestuff of this shade. At the present time, with over two hundred blue dyestuffs on the market, circumstances are completely changed.

and only a systematic method of analysis based upon chemical classification will suffice.

The first proposal for a definite scheme of analysis was made by Witt in 1886,[1] who gave the individual reactions for the colouring-matters then upon the market, and proposed to separate them into groups by their shade, solubility, and behaviour with caustic soda. A more systematic method was published by Weingärtner in the following year.[2] This depended upon the classification of colouring-matters as "acid" and "basic" according as they were precipitated or not by a solution of tannin, and further subdivision by their behaviour upon reduction with zinc-dust.

Faults in the analytical tables of Weingärtner and the appearance of new groups of dyestuffs led the author in 1893 to advance a more comprehensive scheme of analysis.[3] Whilst retaining Weingärtner's system as a foundation, he added additional differentiations which enabled the dyestuffs to be readily divided into chemical classes, thus placing the analysis upon a sure scientific foundation. The general principles of this system are exhibited as follows in Table II.:—

TABLE II.

Decolourised by Zinc-dust.			Unaltered by zinc-dust or only reduced slowly and partially.	Not de-colourised by zinc-dust, but changed in shade completely.
Colour restored on exposure to air.	Colour not restored by air, but returns on treatment with oxidising agents.	Colour not restored either by air or oxidising agents.		
AZINES, OXAZINES, THIAZINES, INDIGOIDS, PYRONES (*VIOLET and BLUE*), ACRIDINES.	TRIPHENYL-METHANE DYES, PYRONES (*RED*).	NITRO, NITROSO, AND AZO DYES.	QUINOLINES, THIAZOLS.	ANTHRACENE DYES.

An alternative scheme, also based upon differences of behaviour towards reducing and oxidising agents, was advanced later by

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[1] Witt, *Chem. Industrie*, 9, 1.

[2] Weingärtner, *Chem. Zeit.*, 1887, pp. 135, 165.

[3] Green, *J. Soc. Chem. Ind.*, 1893, p. 3.

Rota.[1] In the latter scheme stannous chloride and ferric chloride constitute the group reagents; but although useful in certain cases it does not appear to be as reliable as the Green-Weingärtner system.

The above methods of analysis have been further supplemented in recent years by the valuable study of the absorption spectra of dyestuffs made by Formánek,[2] which is at present being continued in co-operation with Grandmougin.[3] Porai-Koschitz and Auschkap have also applied the spectroscopic method to the examination of dyestuffs upon the fibre.[4]

The method for the analysis of dyestuffs in substance, which forms the subject of the present chapter, is based upon the Green-Weingärtner scheme of 1893, which, with the assistance of A. E. Woodhead, has been remodelled to meet the present-day requirements. Since the publication of the original scheme an enormous number of new dyestuffs, and even a few entirely new classes, as, for example, the sulphide colours and the anthracene vat colours, have appeared in commerce. Other classes, such as the indigoid, formerly consisting of only one or two representatives, have been largely extended so that these classes now embrace a large range of dyestuffs of almost all shades. To meet these changes it has been found necessary largely to recast the form of the original tables, although the same general principles are still retained. In the first place, the dyestuffs are grouped by means of their dyeing properties and solubility under four main headings, namely:—

I. Basic dyestuffs and Basic-mordant dyestuffs (precipitated by tannin).
II. Salt and Soluble Sulphide dyestuffs (not precipitated by tannin but dyeing unmordanted cotton).
III. Acid and Acid-mordant dyestuffs (not precipitated by tannin and without affinity for unmordanted cotton).
IV. Insoluble Sulphide, Mordant, Pigment, Spirit, and Vat dyestuffs (insoluble in water).

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[1] Rota, *Chem. Zeit.*, 1898, p. 437.

[2] Formánek, *Spektralanalytischer Nachweis künstlicher organischen Farbstoffe*, 2 Aufl., 1908.

[3] Grandmougin, *Untersuchung und Nachweis organischer Farbstoffe auf spektroscopischem Wege*, 1911.

[4] Porai-Koschitz and Auschkap, "Spektrophotometrische Bestimmung der Farbstoffe auf der Faser," *Zeit. f. Farben-Industrie*, **10**, 293, 321, 342.

The further separation of the components of each of these four main groups is effected, as in the original tables, by making use of their behaviour upon reduction and reoxidation. Instead, however, of the zinc-dust and hydrochloric acid or zinc-dust and ammonia reagents formerly used, zinc-dust with acetic acid is employed; and in place of chromic acid, a very dilute acidified solution of potassium permanganate. By these means greater certainty in the indications is secured. In order to distinguish the soluble "sulphide" dyestuffs from the "salt" dyestuffs in Group II., and the insoluble "sulphide" dyestuffs from the insoluble "mordant" dyestuffs in Group IV., the evolution of hydrogen sulphide upon boiling these colours with stannous chloride is made use of. The same test is employed to distinguish the "vat" colours of the sulphur class from those of the indigoid and anthracene classes, whilst the two latter divisions are differentiated from each other by the colours of their leuco compounds, those of the former being pale yellow, those of the latter dark coloured. The greatest extensions are necessitated in Group IV., which comprises the dyestuffs insoluble in water, since in this table must be included a large body of newly discovered dyestuffs belonging to the "sulphide" and "vat" classes, together with a considerable number of insoluble azo colours employed in the pigment industry.

Unfortunately it is an unavoidable result of the intense activity in dyestuff manufacture which has characterised recent years, that the analytical tables, which were formerly comparatively simple, now contain a large number of members in every division. At the same time a considerable proportion of the names under which dyestuffs appear are synonyms only, and thus the number of individuals is not as great as would appear. Whilst an endeavour has been made to enumerate the most important individual dyestuffs in each category, and even to give as far as possible synonymous designations, it is clear that space will not allow of the insertion of a complete list.

Although in many cases the further subdivision of the members of a division may be effected by the application of individual reactions, the insertion of these tests would have rendered the tables far too unwieldy. Moreover, with the changing state of the industry a complete differentiation into individual products in all cases is "a counsel of perfection" almost impossible to realise. All that can be reasonably expected of a scheme of analysis is that it should render a correct account of the dyeing and chemical relationships of the dyestuffs, and indicate in what direction the equivalent or identical products may be sought.

For distinguishing between the individual dyestuffs falling into any particular division, the reactions towards concentrated sulphuric acid, caustic soda, etc., as given in the new edition of Schultz's tables,[1] are of great service. Considerable assistance may be also derived from a spectroscopic examination of the product carried out in different solvents in the manner described by Formánek,[2] the results obtained being compared with the tables of absorption spectra published by the latter author and by Grandmougin. As a final resort, when the complete identification of the individual dyestuff is sought, the product should be dyed quantitatively upon wool or cotton side by side with the dyestuff with which it is believed to correspond, and a comparison made between the patterns in regard to shade and behaviour with reagents. The complete elucidation of the constitution of an azo dyestuff may be effected by submitting it to reduction or oxidation and isolating its cleavage products (see Chapter IX.). Such a complete examination is, however, as a rule unnecessary; it is usually sufficient for practical purposes to know the class to which the dyestuff belongs.

An obvious alternative to testing dyestuffs in substance consists in dyeing them upon wool or cotton and then proceeding with the identification on the fibre in accordance with the methods described in Chapters V. and VI. This procedure is often conveniently employed as a confirmatory or additional method of analysis.

Reagents.—In carrying out the described scheme the following reagents are employed. It is important that they should be used of the strength indicated.

Tannin Reagent.—Solution of 10 grams of tannin and 10 grams of sodium acetate in 200 c.c. of water.

Zinc-dust.—This must not have been kept too long.

Acid Stannous Chloride.—Solution of 100 grams of stannous chloride in 100 c.c. of pure concentrated hydrochloric acid and 50 c.c. of water.

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[1] Schultz, *Farbstofftabellen*, 5 Aufl., 1914.

[2] Formánek, *loc. cit.*

Lead Acetate.—A 5 per cent. solution in water.

Acid Permanganate.—A solution of 1 gram of potassium permanganate and 2 grams concentrated sulphuric acid in 1000 c.c. of water.

Chromium Fluoride Reagent.—A solution of 10 grams chromium fluoride and 5 grams sodium acetate in 100 c.c. of water.

Alcohol (95 *per cent.*).—Ordinary strong alcohol or methylated spirit.

Caustic Soda (5 *per cent.*).—Solution of 5 grams stick caustic soda in 100 c.c. of water.

Caustic Soda (1 *per cent.*).—The preceding solution diluted five times.

Acetic Acid.—5 c.c. of glacial acetic acid to 95 c.c. of water.

Dilute Formic Acid (1 : 100).—1 c.c. of 90 per cent. formic acid to 100 c.c. of water.

Dilute Hydrochloric Acid.—5 c.c. concentrated hydrochloric acid to 100 c.c. of water.

Dilute Ammonia (1 : 100).—1 c.c. concentrated ammonia diluted with 100 c.c. of water.

Aqueous Alcoholic Ammonia.—1 c.c. concentrated ammonia mixed with 50 c.c. of water and 50 c.c. of alcohol.

Cotton and Wool.—Small pieces about ¾ to 1 inch square (20 to 25 mm. square) of white mercerised cotton and of white woollen cloth (plain and chromed). The chromed wool is prepared by boiling for an hour with 3 per cent. of sodium or potassium bichromate.

Procedure.—*Division into Tables.*—This is effected by ascertaining the solubility of the dyestuff in water and its behaviour towards tannin reagent and with unmordanted cotton. Solubility is to be defined as complete or almost complete solution in boiling water. The tests with tannin and with cotton are carried out with a solution containing approximately 1 part of dyestuff in from 100 to 200 parts of water. A similar solution is used for the reduction tests. In performing the cotton test a small piece of white mercerised cotton, about ¾ inch square, is boiled in a test-tube for half a minute with the dyestuff solution. The cotton is then removed and boiled for one minute with dilute ammonia (1 : 100). The latter treatment is necessary in order to remove any stain upon the cotton which might be produced by "acid" dyestuffs. In reference to this test it should be borne in mind that the distinction between "salt" and "acid" dyes is not an absolute one, since some products usually regarded as "acid" dyestuffs have a weak affinity for cotton.

Preliminary Tests.—Before proceeding to further differentiation, it is advisable to test the dyestuff for metallic compounds by ignition, flame reactions, borax beads, etc. In the case of a soluble dyestuff, chromium and copper in particular should be looked for, and their presence would suggest an "acid-mordant" dyestuff in association or combination with a mordant. Dyestuffs of this type are represented, for example, by the Erganone series, the Mercerol series, the Phenochrome colours, and by Fast Acid Red RH, Fast Acid Bordeaux BH, and Erio Fast Blue SWR. The presence of a considerable quantity of mineral matter, especially compounds of barium, calcium, aluminium, or lead, associated with an insoluble dyestuff would indicate a lake pigment. In such cases the examination should be conducted in accordance with the methods described in Chapter VIII.

Differentiation by Reduction and Oxidation.—The reduction with zinc-dust requires to be performed with some care. It is usually best to add a little zinc-dust, sufficient to cover the tip of a penknife, to the hot solution of the colouring-matter contained in a test-tube; agitate, and then add a few drops of acetic acid (5 per cent.) until decolourisation occurs. In the case of some "basic" colouring matter a deficiency of acetic acid may lead to precipitation of the leuco base, and consequent failure of the subsequent reoxidation. The solution when reduced is poured off from the greater part of the zinc-dust on to a piece of white filter-paper and exposed to air; filtration is unnecessary, as a little zinc-dust upon the paper has no injurious effect. If the colour does not return in a minute or two, the paper is touched with a glass rod dipped in the acid permanganate solution. Warming gently over a flame facilitates the oxidation. In the case of red "acid" colouring-matters, the paper, after spotting with permanganate, should be held over a bottle of strong ammonia, for a few "acid" colouring-matters (*e.g.* the Eosines) do not show their true colour whilst acid. Moreover, in the case of Eosines containing iodine a brown spot of the latter may be formed with permanganate, but this disappears on exposure to ammonia vapour, leaving the correct colour of the dyestuff.

Great care must be taken that one is not led astray by secondary colourations produced by the oxidation of the diamines and amidophenols obtained upon reduction of azo colouring-matters.

Distinction between Acid and Acid-mordant Dyestuffs.—Chromed and unchromed pieces of wool (about 1 inch square) are well wetted out and are placed in a large test-tube with a small amount of the dyestuff solution, together with water and one or two drops of dilute formic acid (1 : 100). The test-tube is heated to boiling, and then immersed in a beaker of boiling water for a quarter of an hour in order to enable the mordant to completely fix the dyestuff. The patterns are then boiled with dilute ammonia (1 : 100), and the degree of stripping observed by the loss of colour which the pattern undergoes. In the case of black dyestuffs, aqueous alcoholic ammonia should be substituted for the aqueous ammonia.

Distinction between Basic and Basic-mordant Dyestuffs.—The mordant dyestuffs of the oxazine class, since they also contain basic groups, are precipitated by tannin and hence fall into Table IV. In order to distinguish them from the true "basic" dyestuffs, their behaviour towards chromium salts, *e.g.* a solution of chromium fluoride and sodium acetate, is made use of. With this reagent only those basic dyestuffs give precipitates which contain mordant-dyeing (hydroxyl) groups.

Test for Sulphide Dyestuffs and Sulphur Vat Colours.—A small quantity of the solid dyestuff is placed in a test-tube and covered with acid stannous chloride solution. The mouth of the test-tube is closed by a cap of filter-paper closely wrapped round it, and into the centre of this is placed, by means of a glass rod, one drop of lead acetate solution. The contents of the test-tube are slowly heated just to boiling, when a blackish-brown stain of lead sulphide appears. The brown spot will again disappear upon boiling the solution longer, owing to the decomposition of the lead sulphide by the hydrochloric acid evolved. The test requires some practice, as small quantities of hydrogen sulphide may be evolved from other sources (impurities in the dyestuffs, etc.). It should be noted that it is not sufficient to obtain a yellow or pale brown spot; only a deep brown of almost black and iridescent appearance can be regarded as a positive indication.

Differentiation by Colour.—The colour designations heading certain columns in the tables are to be taken to mean the shade of the dyestuff in aqueous solution. This is frequently not the same as the dyed shade, from which the dyestuff receives its name. Thus, for example, several brands of greens and blues of the "acid-mordant" class are to be found in Table VI. in the column headed "Violet," this being the colour of their aqueous solutions.

Reduction Test for Vat Dyestuffs.—A small quantity of the powder sufficient to cover the tip of a penknife, or the equivalent amount of a paste, is placed in a test-tube together with a little 1 per cent. caustic soda solution and as much solid sodium hydrosulphite BASF as of powder. The mixture is warmed to about 80° for five or ten minutes. Vat dyestuffs are dissolved and the colour of the solution is an indication of the constitution, those of the indigoid class giving pale yellowish solutions, whilst those of the anthracene class give more or less deeply coloured solutions. As confirmatory tests it may be mentioned that nearly all the dyestuffs of the indigoid class, and also some of the anthracene class, are soluble in boiling benzene; and that the indigoid colours sublime on heating, forming coloured vapours, whilst the vat colours of the anthracene class, with a few exceptions, do not. The vat dyestuffs of the sulphur class are insoluble in benzene and do not sublime on heating.

Identification of Bisulphite Compounds.—Certain insoluble mordant dyestuffs are rendered soluble in water by combination with sodium bisulphite, for example the S marks of Alizarine Blue, Alizarine Green, Alizarine Black, and Cœruline. They are distinguished from ordinary "acid-mordant" dyestuffs (sulphonic acids) by the evolution of sulphurous acid upon boiling with dilute hydrochloric acid. Upon reduction with acid stannous chloride these compounds evolve hydrogen sulphide, and hence might be confused with sulphide dyestuffs.

Detection of Halogens.—The presence of halogens in the nucleus of organic dyestuffs, for example bromine in Ciba Blue and in Eosine, and iodine in Rose Bengal, may be detected by heating the dyestuff with concentrated sulphuric acid and manganese dioxide.

Distinction between Sulphonated and Unsulphonated (Phenolic) Acid Dyestuffs.—This is effected by shaking the acidified solution with ether, in which only the dyestuffs of the latter type (for example the Eosines) are soluble.

Mixtures.—A considerable proportion of the dyestuff brands occurring in commerce are mixtures of two or more products. When one of these products is present in small quantity only, being added by way of a shading constituent, the reactions of the main product may not be appreciably obscured. Also in the very frequent cases in which the mixed dyestuffs belong to the same chemical class, no difficulty in ascertaining this class will be presented. If, however, the mixture consists of products belonging to different classes, a separation of the constituents should be attempted. The following methods are available for the recognition of mixtures, and in some cases for their separation.

Sprinkling Test.—(1) A little of the solid dyestuff held upon the tip of a penknife or on a small card is blown suddenly over a piece of wet filter-paper placed in front. Upon examining the paper, streaks of varying hue will be discerned if the product is a mixture of dyestuffs differing considerably in shade. If the result is negative the experiment should be repeated with filter-paper moistened with alcohol instead of with water. (2) A very little of the powder is lightly dusted over the surface of concentrated sulphuric acid contained in a clean white porcelain dish, and the colour of the separate dissolving particles is carefully noted. Owing to the fact that many dyestuffs dissolve in concentrated sulphuric acid with very characteristic colours, which are often quite different from that of their aqueous or alcoholic solutions, mixtures may be frequently detected which are unrecognisable by sprinkling on paper. For example, a mixture of a Xylidine Scarlet with a Crocein Scarlet could be readily detected owing to the fact that the first dissolves in concentrated sulphuric acid with a red colour, the latter with a blue colour; although in water they have nearly the same shade.

Capillarity Test.—The extent to which dyestuffs diffuse upon filter-paper varies considerably, and upon these differences Goppelsroeder has based a method of distinction and separation which is of frequent service. The solution of the mixed dyestuffs is allowed to drop from a pipette upon thick filter-paper, when the formation of two or more coloured zones may often be observed. These zones can be further separated by subsequently allowing one or two drops of distilled water to fall into the centre of the spot. After drying, each zone is cut out and extracted with water. Another method consists in allowing strips of filter-paper to hang over glass rods with their lower ends dipping into the dye solution, the whole being covered with a glass bell-jar. The constituent dyestuffs then rise by capillary attraction to varying heights upon the paper strips.

Separation by Solvents.—Use can be often made of differences in solubility in the constituents of a mixture towards various organic solvents, such as alcohol, amyl alcohol, chloroform, ether, benzene, etc. The substance may either be extracted in the solid state, *e.g.* with alcohol, or the aqueous solution may be shaken out with an immiscible solvent. For example, a mixture of soluble Nigrosine and Metanil Yellow (used for colouring boot-creams) is readily separated by extracting the powdered dyestuff with 95 per cent. alcohol, which dissolves the Yellow and leaves the Nigrosine. In extractions from the aqueous solution with a solvent such as ether (a method recommended by Rota) the state of acidity or alkalinity of the solution may be employed as a basis of separation. Thus phenolic dyestuffs (Eosines, Martius Yellow, etc.) are extracted from an acidified solution, "basic" dyestuffs from an alkaline solution, "acid" dyestuffs containing sulphonic groups usually not at all. Again, owing to the varying facility with which the free bases are liberated from their salts, a separation can be effected, for example, of a mixture of the three "basic" dyestuffs Rhodamine, Magenta, and Safranine. Upon shaking the aqueous solution of this mixture with ether, the Rhodamine base is extracted (giving a colourless ethereal solution). On then adding ammonia and extracting again, the Magenta base is taken up. Finally, the residual aqueous solution gives up the Safranine base to ether after addition of caustic soda.

Separation by Dyeing.—The separation of "acid" dyestuffs can frequently be effected by fractional dyeing upon wool or silk from the aqueous solution acidified with acetic or formic acid. A large number of small pieces of wool are dyed in succession from the solution until the colour is exhausted. All those patterns which have the same shade, are extracted together by boiling dilute ammonia (1 : 100); the solution so obtained is again dyed upon wool and the operation repeated. The extraction is also carried out fractionally, the residual colour being separately extracted and redyed.

Separation by Adsorption.—It has long been known that materials such as kaolin, kieselguhr, asbestos, etc., exert an affinity for certain colouring-matters. Upon this fact Chapman and Siebold[1] have based a method of separation. The dyestuff solution. about 1 gram per 1000 c.c., is shaken with kaolin (china clay), using 5 grams of the latter to 20 c.c. of the solution, and the mixture is then filtered upon a Büchner funnel. The behaviour of some typical dyestuffs is given in Table III.

TABLE III.

Precipitated on the kaolin.	Partially taken up by the kaolin, but in part redissolved on washing with water.	Not precipitated.
CONGO RED, SAFRANINE, MAGENTA, NEUTRAL RED, MALACHITE GREEN, BRILLIANT GREEN, METHYLENE BLUE, BISMARCK BROWN, CRYSTAL VIOLET, METHYL VIOLET, AURAMINE.	ACID GREEN, PATENT BLUE, SOLUBLE BLUE	ACID MAGENTA, EOSINE, ERYTHROSINE, FLUORESCEIN, METHYL ORANGE, ORANGE II., ORANGE IV., PONCEAU 4R, BORDEAUX R, TARTRAZINE, NAPHTHOL YELLOW, NAPHTHOL GREEN, INDIGO CARMINE

Detection of Artificial Dyestuffs in Articles of Food.

At the present time artificial dyestuffs are very largely used for the colouring of various dietic products, such as jams, jellies, fruit syrups, beer, liqueurs, lemonade, confectionery, cakes, milk, butter, margarine, cream, cheese, macaroni, dried fish, sausages, etc. Whilst in some countries, as, for example, the United States, only an approved list of selected dyestuffs is permitted, in other countries certain specified dyestuffs alone are forbidden, and in others, again, there is no legal restriction. Expert opinions differ widely as to how far artificial dyestuffs are injurious to health, and even as to which dyestuffs are objectionable.[2] Experiments seem to show, however, that only those dyestuffs which are basic in character (such as Safranine), and those containing nitro groups, can be

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[1] Chapman and Siebold, *Analyst*, 1912, p. 339.

[2] Hesse, *Coal-tar Colours used in Food Products* (Bull. U.S. Department of Agriculture, No. 147, 1912).

regarded as definitely toxic, whilst the introduction of sulphonic groups mainly or entirely removes this toxicity. It may therefore be safely asserted that "acid" dyestuffs containing sulphonic groups, with few if any exceptions, are harmless for dietic purposes when used in the small quantities required. It is, however, desirable that dyestuffs employed for colouring food should be free from mineral impurities such as lead and arsenic, which are occasionally found in considerable quantities in commercial dyestuffs.

The investigation of dyestuffs present in articles of diet is best effected by transferring the dye to white wool, which in the case of "acid" dyestuffs (with which one is mainly concerned) can usually be readily effected. Employing the procedure of Sestegni and Carpentieri[1] the operation is conducted as follows:—100 c.c. of the coloured liquid (alcohol if present having been boiled off), or 50 grams of the solid or semi-solid material mixed with an equal weight of water, is acidified with 1 c.c. of concentrated hydrochloric acid and gently boiled for five or ten minutes with a small piece of white woollen cloth. The wool is rinsed in water and (in order to remove vegetable colours) is warmed for a few minutes with very dilute hydrochloric acid. It is then boiled for two or three minutes with dilute ammonia (1 : 100), which extracts the "acid" dyestuff, leaving a small amount of vegetable colour behind on the fibre. The coloured solution obtained is acidified with hydrochloric acid and boiled with a second piece of wool smaller than the first. The dyed wool may then be subjected to identification tests in the manner described in Chapter V., or the colour may be again stripped with ammonia and the dyestuff examined in solution. If the colour is still insufficiently pure, the transference to wool and restripping may be again repeated.

The presence of Eosines, Phloxines, etc., in food materials, such, for example, as preserved cherries, may be readily ascertained by acidifying the material and extracting it directly with ether or chloroform. On evaporation of the solvent and rendering alkaline with ammonia the Eosine is obtained, and can be further identified by the usual tests and by dyeing on silk.

Basic dyestuffs in food materials are identified by transferring to tannin-mordanted cotton and afterwards removing from the cotton by treatment with saline caustic soda in the manner described

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[1] Sestegni and Carpentieri, *Zeitsch. Anal. Chem.*, 1889, **28**, 639.

in Chapter VI. They may also be extracted from the articles with ether, after rendering alkaline with caustic soda. The ether solution is then acidified with acetic acid and evaporated to dryness.

The presence of unsulphonated nitro compounds (such as Picric Acid, Victoria Yellow, and Martius Yellow) may be detected in dry materials, such as biscuits, etc., by heating the material with an iron in close contact with white paper. These dyestuffs being volatile will then stain the paper yellow.

TABLE IV.—BASIC AND BASIC-MORDANT DYESTUFFS.

SOLUBLE in WATER. PRECIPITATED by TANNIN REAGENT.

Reduce with zinc-dust and acetic acid.																
The solution is decolourised, and the colour returns on exposure to air. The colour of the aqueous solution is:—							The solution is decolourised, and a pink colour returns on exposure to air: **Safranine Azo Class.**	The solution is decolourised, and the colour returns on spotting with acid permanganate: **Triphenylmethane** and **Pyrone Classes.** The colour of the aqueous solution is:—				The solution is decolourised, and the colour does not return either in air or with acid permanganate: **Azo Class.** The colour of the aqueous solution is:—			Colour unaltered: **Thiazols** and **Ketonimides.** On boiling with zinc-dust and dilute hydrochloric acid:—	
Red: **Azine Class.**	Orange and yellow: **Acridine Class.**	Green: **Thiazine Class.**	Blue: **Oxazine** or **Thiazine.**		Violet: **Oxazine** or **Azine.**											
			On the addition of chromium fluoride reagent to a solution of the dyestuff.		On the addition of chromium fluoride reagent to a solution of the dyestuff.											
			Colour precipitated: **Basic-mordant Dyestuff.**	No precipitate: **Basic Dyestuff.**	Colour precipitated: **Basic-mordant Dyestuff.**	No precipitate: **Basic Dyestuff.**		Red.	Green.	Blue.	Violet.	Red.	Orange and yellow.	Brown.	Solution is slowly decolourised.	Solution is slowly decolourised, and on further boiling becomes blue-violet.
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.	17.
INDULINE SCARLET, SAFRANINE, BRILLIANT SAFRANINE, ROSOLANE, NEUTRAL RED, RHODULINE RED, BRILLIANT RHODULINE RED.	ACRIDINE YELLOW, ACRIDINE ORANGE, PHOSPHINE, RHEONINE, PATENT PHOSPHINE, DIAMOND PHOSPHINE, FLAVOPHOSPHINE, CORIPHOSPHINE, HOMOPHOSPHINE, BRILLIANT PHOSPHINE, AURACINE, RHODULINE ORANGE, BENZOFLAVINE, CORIOFLAVINE, AUROPHOSPHINE.	METHYLENE GREEN, AZINE GREEN.	CELESTINE BLUE, COREINE 2R, ULTRA CYANINE, MODERN CYANINE, PHENOCYANINE, CHROMOCYANINE.	METHYLENE BLUE, NEW METHYLENE BLUE, THIONINE BLUE, CAPRI BLUE, CRESYL BLUE, BRILLIANT CRESYL BLUE, NILE BLUE, BASLE BLUE, MELDOLA'S BLUE, FAST NAVY BLUE, NEW BLUE, METAMINE BLUE, NAPHTHOL BLUE, METAPHENYLENE BLUE, PARAPHENYLENE BLUE, INDAMINE BLUE, INDAZINE, NEUTRAL BLUE, MUSCARINE, DIPHENE BLUE, RHODULINE BLUE, RHODULINE SKY BLUE.	ULTRA VIOLET, MODERN VIOLET, MODERN HELIOTROPE, PRUNE.	PARAPHENYLENE VIOLET, RHODULINE VIOLET, RHODULINE HELIOTROPE, METHYLENE VIOLET, METHYLENE HELIOTROPE, TANNIN HELIOTROPE, IRIS VIOLET, AMETHYST VIOLET, CRESYL FAST VIOLET.	INDONE BLUE, NAPHTHINDONE, JANUS BLUE, JANUS DARK BLUE, JANUS GREEN, JANUS BLACK, JANUS GREY, DIAZINE BLUE, DIAZINE GREEN, DIAZINE BLACK, DIAZINE BROWN, BRILLIANT DIAZINE BLUE, INDOINE BLUE, INDOLE BLUE.	PYRONINES, ACRIDINE RED, RHODAMINES, RHODINES, IRISAMINE, MAGENTA, NEW FUCHSINE, ISORUBINE.	MALACHITE GREEN, BRILLIANT GREEN, DIAMOND GREEN, FAST GREEN, NEW FAST GREEN, METHYL GREEN, ETHYL GREEN, IODINE GREEN, VICTORIA GREEN, NEW VICTORIA GREEN, CHROME GREEN.	NIGHT BLUE, VICTORIA BLUE, NEW VICTORIA BLUE, BRILLIANT VICTORIA BLUE, VICTORIA PURE BLUE, GLACIER BLUE, BRILLIANT GLACIER BLUE, SETOCYANINE, SETOGLAUCINE, SETOPALINE, TURQUOISE BLUE, RHODULINE BLUE 5B, 6G, CHROME BLUE.	CRYSTAL VIOLET, METHYL VIOLET, BRILLIANT VIOLET, ETHYL PURPLE, BENZYL VIOLET, HOFMANN'S VIOLET, CHROME VIOLET.	ROSOLE RED, ROSOLE SCARLET, JANUS RED, DIAZINE RED.	CHRYSOIDINE, NEW PHOSPHINE, AZO PHOSPHINE, TANNIN ORANGE, JANUS YELLOW.	BISMARCK BROWN, VESUVINE, PHENYLENE BROWN, JANUS BROWN, TANNIN BROWN.	THIOFLAVINE T, METHYLENE YELLOW, RHODULINE YELLOW.	AURAMINE.

TABLE V.—SALT AND SULPHIDE DYESTUFFS.

SOLUBLE in WATER. NOT PRECIPITATED by TANNIN REAGENT. DYE COTTON DIRECTLY.

Apply stannous chloride and lead acetate test.								
A deep brown stain is produced: **Sulphide Class.**	Little or no brown stain is produced: **Salt Dyestuff.** Reduce with zinc-dust and acetic acid.							
	Colour reduces very slowly and incompletely: **Thiazol Class.**	Decolourised. Colour returns in air: **Stilbene Class.**	Decolourised. Colour does not return in air: **Azo Class.** The colour of the aqueous solution is:—					
			Red.	Yellow, orange, and brown.	Green.	Blue.	Violet.	Black.
1.	2.	3.	4.	5.	6.	7.	8.	9.
WATER-SOLUBLE SULPHIDE COLOURS OF THE AURANOL, CROSS-DYE, ECLIPSE, IMMEDIAL, KATIGEN, KRYOGENE, PYROGENE, PYROL, SULPHUR, THIOGENE, THION, THIONAL, THIONOL, AND THIOXINE SERIES. REXOLL BLACK.	PRIMULINE, SULPHINE, THIOFLAVINE S, THIAZOL YELLOW, CLAYTON YELLOW, CHLORAMINE YELLOW, BRILLIANT PURE YELLOW, CHLORAZOL FAST YELLOW, DIAMINE FAST YELLOW B, 2F, M, CHLOROPHENINE, ORIOL YELLOW, MIMOSA YELLOW, COLUMBIA YELLOW, NITROPHENINE, TRIAZOL FAST YELLOW, DIANIL PURE YELLOW, NAPHTHAMINE PURE YELLOW, OXYDIAMINE YELLOW, OXYDIANIL YELLOW.	DIRECT YELLOW, NAPHTHAMINE YELLOW, MIKADO YELLOW, MIKADO GOLDEN YELLOW, MIKADO ORANGE, SUN YELLOW, CURCUMINE S, STILBENE YELLOW, DIAMINE FAST YELLOW A, CHLORAMINE ORANGE, DIPHENYL FAST YELLOW, DIPHENYL CHRYSOIN, DIPHENYL CITRONINE, POLYPHENOL YELLOW, DIAMINE ORANGE D, STILBENE ORANGE.	PINKS, REDS, FAST REDS, SCARLETS, FAST SCARLETS, BRILLIANT SCARLETS, GARNETS, BORDEAUX, CLARETS, CORINTHS, RUBINES AND MAROONS OF THE BENZO, BENZOFORM, CHLORAMINE, CHLORANTINE, CHLORAZOL, COLUMBIA, CONGO, COTTON, DIAMINE, DIANIL, DIANOL, DIAZANIL, DIAZO, DIPHENYL, DIRECT, FORMAL, GLYCINE, HESSIAN, NAPHTHAMINE, OXAMINE, OXYDIAMINE, PARA, PARANIL, ROSANTHRENE, SULTAN, TITAN, TOLUYLENE, ETC., SERIES. AUTOCHROME RED, ACETOPURPURINE, ANTHRACENE RED, AZO PURPURINE, BENZO FAST EOSINE, BENZOPURPURINE, BRILLIANT PURPURINE, DELTAPURPURINE, DIAZO GERANINE, ERIKA, GERANINE, ROSANOL, ROSAZURINE, SOLAMINE RED, ROSOPHENINE, TRONA RED.	YELLOWS, ORANGES, CATECHINS, BROWNS, DARK BROWNS, ETC., OF THE BENZO, BENZOFORM, CATECHU, CHICAGO, CHLORAZOL, CONGO, COTTON, CUPRANIL, DIAMINE, DIANIL, DIAZO, DIPHENYL, HESSIAN, NAPHTHAMINE, OXAMINE, OXYDIAMINE, PARA, PARANIL, PLUTO, PYRAMINE, RENOL, TOLUYLENE, TRISULPHON, ZAMBESI, ETC., SERIES. AUTOCHROME ORANGE, BRILLIANT ORANGE, BRILLIANT YELLOW, CHRYSAMINE, CHRYSOPHENINE, CRESOTINE YELLOW, CUTCH BROWNS, DIAMINE GOLD, DIRECT BROWNS, POLAR YELLOW R CONC., POLAR ORANGE, POLAR RED.	GREENS, DARK GREENS AND OLIVES OF THE AZIDINE, BENZO, CHLORAMINE, CHLORANTINE, CHLORAZOL, COLUMBIA, DIAMINE, DIANIL, DIANOL, DIAZO, DIPHENYL, DIRECT, EBOLI, NAPHTHAMINE, OXAMINE, PARA, PARANIL, RENOL, TRIAZOL, ETC., SERIES.	BLUES, SKY BLUES, BRILLIANT BLUES, PURE BLUES, DARK BLUES, NEW BLUES, FAST BLUES, STEEL BLUES, NAVY BLUES, INDIGO BLUES, BLUE BLACKS, CYANINES, AZURINES, ETC., OF THE BENZO, BENZOFORM, CHICAGO, CHLORAMINE, CHLORANTINE, CHLORAZOL, COLUMBIA, CONGO, COOMASSIE, COTTON, DIAMINE, DIAMINERAL, DIANIL, DIANOL, DIAZANIL, DIAZO, DIPHENYL, DIRECT, EBOLI, FORMAL, HESSIAN, INDIGENE, NAPHTHAMINE, NAPHTHOGENE, OXAMINE, OXYCHLORAZOL, PARA, POLYPHENOL, RENOL, SOLAMINE, SULPHON, TOLUYLENE, ZAMBESI, ETC., SERIES. AUTOCHROME BLUE B, CUPRAMINE BRILLIANT BLUE, DIAMINOGEN, DIAZURINE, INDAZURINE, METAZURINE, NAPHTHAZURINE, OXYDIAMINOGEN, SULPHONCYANINES, TOLYL BLUE GR AND 5R.	VIOLETS AND HELIOTROPES OF THE BENZO, BENZOFORM, BRILLIANT CONGO, CHLORAMINE, CHLORAZOL, COLUMBIA, DIAMINE, DIANIL, DIANOL, DIAZO, DIPHENYL, DIRECT, FORMAL, NAPHTHAMINE, OXAMINE, OXYDIAMINE, PARA, ROSANTHRENE, TRISULPHON, ETC., SERIES. AZO MAUVE, AZO VIOLET, BENZO FAST HELIOTROPE, CHLORANTINE LILAC, HESSIAN PURPLE.	BLACKS, FAST BLACKS, JET BLACKS, DEEP BLACKS, GREYS, ETC., OF THE BENZO, CHLORAMINE, CHLORAZOL, COLUMBIA, COOMASSIE, COTTON, DIAMINE, DIAMINERAL, DIANIL, DIANOL, DIAZANIL, DIAZO, DIPHENYL, DIRECT, FORMAL, INDIGENE, INGRAIN, ISODIPHENYL, NAPHTHAMINE, OXAMINE, OXYDIAMINE, PARA, PARADIAMINE, PARANIL, PLUTO, PLUTOFORM, RENOL, TITAN, TOLUYLENE, ZAMBESI, ETC., SERIES. DIAMINE NERON, MELANTHERIN.

TABLE VI.—ACID AND ACID-MORDANT DYESTUFFS.

SOLUBLE in WATER. NOT PRECIPITATED by TANNIN REAGENT. DO NOT DYE COTTON DIRECTLY.

Reduce with zinc-dust and acetic acid.				
Colour unaltered: Quinoline Class.			1.	QUINOLINE YELLOW, QUINALDINE YELLOW.
Decolourised. Colour returns in air: Azines, Thiazines, Oxazines, and Pyrones.			2.	FAST ACID VIOLET, FAST ACID RED A, FAST ACID BLUE R CONC., VIOLAMINE, INDULINE w.s., FAST BLUE, SOLID BLUE, NIGROSINE w.s., SILVER GREY, ROSINDULINE, AZO CARMINE, NAPHTHYL BLUE, INDOCHROMINE, BRILLIANT ALIZARINE BLUE, THIOCARMINE, ALIZARINE GREEN B, G, DELPHINE BLUE, BRILLIANT DELPHINE BLUE, LANOGLAUCINE, CHROMAZURINE, LAZULINE BLUE, ACID CYANINE, WOOL FAST BLUE, WOOL FAST VIOLET, INDIGO CARMINE.
Decolourised. Colour returns on spotting with acid permanganate: Triphenylmethane and Pyrone Classes. Acidify the aqueous solution, and shake with ether.	Ether layer is coloured.		3.	FLUORESCEINE, URANINE, EOSINE, PHLOXINE, ERYTHROSINE, ROSE BENGALE, METHYL EOSINE, EOSINE SCARLET, CYANOSINE, METACHROME VIOLET.
	Ether layer is colourless.		4.	FAST ACID EOSINE, FAST ACID PHLOXINE, FAST ACID MAGENTA, ACID ROSAMINE, ACID RHODAMINE, SULPHO ROSAZEINE, XYLENE RED, BRILLIANT KITONE RED, CHROMORHODINE, ACID MAGENTA, ACID VIOLETS, ALKALI VIOLETS, FORMYL VIOLET, GUINEA VIOLET, KITONE VIOLET, FAST ACID VIOLET 10B, PATENT BLUES, ERIOGLAUCINE, ERIOCYANINE, NEPTUNE BLUE, XYLENE BLUE, KITONE BLUE, BRILLIANT ACID BLUE, CYANOLE, CYANINE, ALKALI BLUES, SOLUBLE BLUES, WATER BLUES, METHYL BLUES, WOOL BLUE, BRILLIANT MILLING BLUE, ISAMINE BLUE, BRILLIANT DIANIL BLUE, BRILLIANT CHLORAZOL BLUE, ACID GREENS, GUINEA GREEN, NEPTUNE GREEN, BRILLIANT MILLING GREEN, ERIOVIRIDINE, LIGHT GREEN, WOOL GREEN, AGALMA GREEN, NAPHTHALENE GREEN, CYANOL GREEN, ALKALI FAST GREEN.
Decolourised. Colour does not return either in air or with acid permanganate: Azo Class (also Nitro and Nitroso). Boil small pieces of chromed and unchromed wool in the dye solution with a few drops of formic acid (1 : 100). Wash thoroughly, and boil with ammonia (1 : 100).	Colour stripped from both patterns: Acid Dyestuff. Colour of solution is:—	Red.	5.	ACETYL RED, AMARANTH, AMIDO NAPHTHOL RED, ANTHOSINE, AZO ACID CARMINE, AZO ACID RED, AZO COCCINE, AZO EOSINE, AZO FUCHSINE, AZO MILLING RED, AZO RUBINE, BIEBRICH ACID RED, BIEBRICH SCARLET, BORDEAUX, BRILLIANT ACID CARMINE, BRILLIANT COCHINEAL, BRILLIANT CROCEINE, BRILLIANT DOUBLE SCARLET, CHROMAZONE RED, CROCEINE SCARLET, CRYSTAL SCARLET, EOSAMINE, ERIOCARMINE, ERIOFLOXINE, ERIORUBINE, FAST RED, GUINEA RED, LANAFUCHSINE, NAPHTHOL RED, PALATINE SCARLET, PONCEAU, SORBINE RED, SUPRAMINE RED, VICTORIA SCARLETS, WOOL REDS, WOOL SCARLETS, LITHOL REDS, LAKE REDS.
		Yellow, orange, or brown.	6.	MARTIUS YELLOW, NAPHTHALENE YELLOW, ACID YELLOW, CITRONINE, NAPHTHOL YELLOW, TARTRAZINE, TARTRAPHENINE, XYLENE YELLOW, GUINEA FAST YELLOW, FAST LIGHT YELLOW, KITONE YELLOW, FAST ACID YELLOW, INDIAN YELLOW, SUPRAMINE YELLOW, SULPHON YELLOW, FAST YELLOW, AZO FLAVINE, BRILLIANT YELLOW, PALATINE LIGHT YELLOW, AZO ACID YELLOW, NORMAL YELLOW, PHENOFLAVINE, VICTORIA YELLOW, METANIL YELLOW, ORANGE II., IV., ETC., FAST LIGHT ORANGE, WOOL FAST ORANGE, FAST ACID ORANGE, SULPHON ORANGE, BRILLIANT ORANGE, CROCEINE ORANGE, ACID BROWN, FAST BROWN, SULPHON ACID BROWN, RESORCINE BROWN, SUPRAMINE BROWN, GUINEA BROWN, NEPTUNE BROWN, WOOL BROWN.
		Green.	7.	SULPHON ACID GREEN, NAPHTHOL GREEN B.
		Blue.	8.	AZO ACID BLUE, AZO CYANINE, AZO MERINO BLUE, AZO NAVY BLUE, BRILLIANT CLOTH BLUE, CHROMAZONE BLUE, DOMINGO BLUE BLACK, ERIO FAST BRILLIANT BLUE, ETHYL ACID BLUE, CRESOL BLUE BLACK, LANACYL BLUE, NAPHTHOL BLUE BLACK, NAPHTHYLAMINE BLUE BLACK, ORTHOCYANINE, PHENYL BLUE BLACK, SULPHON ACID BLUE, TOLYL BLUE SB, SR, ST.
		Violet.	9.	AZO ACID VIOLET, ANTHOSINE VIOLET, DOMINGO VIOLET, ERIO FAST PURPLE, ETHYL ACID VIOLET, FAST SULPHON VIOLET, INDO VIOLET, LANACYL VIOLET, OMEGA LIGHT CLARET, OMEGA LIGHT VIOLET, SULPHON VIOLET, VICTORIA VIOLET, WOOL VIOLET.
		Black.	10.	ACID BLACK, AGALMA BLACK, ALPHANOL BLACK, AMIDO ACID BLACK, AMIDO NAPHTHOL BLACK, AMIDO BLACK, ANTHRACITE BLACK, AZO ACID BLACK, AZO MERINO BLACK, BIEBRICH PATENT BLACK, BRILLIANT BLACK, COOMASSIE WOOL BLACK, ETHYL BLACK, FAST SULPHON BLACK, GUINEA BLACK, KRESOL BLACK, NAPHTHALENE ACID BLACK, NAPHTHOL BLACK, NAPHTHYLAMINE BLACK, NEROL, ORTHO BLACK, PALATINE BLACK, PHENOL BLACK, PHENYLAMINE BLACK, SULPHON ACID BLACK, SULPHONCYANINE BLACK, SUPRAMINE BLACK, TOLYL BLACK, VICTORIA BLACK, WOOL BLACK.
	Little or no colour is stripped from the chromed pattern: Acid-mordant Dyestuff. Colour of solution is:—	Red.	11	ACID CHROME RED, ACID ANTHRACENE RED, ACID ALIZARINE RED, ANTHRACENE CHROME RED, ACID ALIZARINE GARNET, AZO ALIZARINE CARMOISINE, CHROME FAST BORDEAUX, CHROME FAST GARNET, CHROMOTROPES, DIAMOND RED, ERIOCHROME RED, ERIOCHROME BORDEAUX, OMEGA CHROME RED, OXYCHROME GARNET, PALATINE CHROME RED, ERIOCHROME OLIVE, PALATINE CHROME VIOLET, ANTHRACENE CHROME VIOLET, ACID CHROME BLUE, AZO CHROME BLUE, CHROME FAST BLUE, CHROMOTROPE BLUE, OMEGA CHROME BLUE.
		Yellow, orange, or brown.	12.	ACID ALIZARINE BROWN, ACID ANTHRACENE BROWN, ALIZADINE BROWN, ANTHRACENE ACID BROWN, ANTHRACENE CHROME BROWN, CHROMAL BROWN, CHROME FAST BROWN, CHROMOXANE BROWN, ERIOCHROME BROWN, MONOCHROME BROWN, OXYCHROME BROWN, PALATINE CHROME BROWN, SALICINE CHROME BROWN, SALICINE RED BROWN, ACID CHROME YELLOW, ALIZADINE ORANGE, ALIZARINE YELLOWS, ANTHRACENE ORANGE, ANTHRACENE YELLOW, AZO ALIZARINE ORANGE, AZO ALIZARINE YELLOW, CHROME FAST YELLOW, CHROMOCITRONINE, CHROME YELLOW, CHROME ORANGE, DIAMOND ORANGE, ERIOCHROME YELLOW, ERIOCHROME PHOSPHINE, METACHROME YELLOW, MORDANT YELLOW, SALICINE ORANGE.
		Green.	13.	CHROME GREEN G.
		Blue.	14.	CHROME CYANINE, CHROME FAST CYANINE, METACHROME BLUE, PALATINE CHROME BLUE.
		Violet.	15	ACID ALIZARINE GREEN 2B, ACID CHROME GREEN, CHROME FAST GREEN, DIAMOND GREEN, ERIOCHROME GREEN, FAST CHROME GREEN P, OMEGA CHROME GREEN, CYPRUS GREEN, OXYCHROME VIOLET, ERIOCHROME VIOLET, ACID ALIZARINE VIOLET, CHROME FAST VIOLET, MONOCHROME BLUE, OXYCHROME BLUE, SALICINE CHROME BLUE, SALICINE INDIGO BLUE.
		Black.	16	ACID ALIZARINE BLACK, ACID CHROME BLACK, ANTHRACENE ACID BLACK, ANTHRACENE CHROME BLACK, CHROMATE BLACK, CHROME ACID BLACK, CHROME FAST BLACK, DIAMOND BLACK, ERIOCHROME BLACK, FAST CHROME BLACK, FAST MORDANT BLACK, MONOCHROME BLACK, OMEGA CHROME BLACK, OXYCHROME BLACK, PALATINE CHROME BLACK, SALICINE BLACK.
Not decolourised, but changed in shade: Anthracene Class. The colour of the reduced solution is	Red.		17	ALIZARINE CYANOL EF, ALIZARINE SAPHIROL, ALIZARINE DIRECT CYANINE, ALIZARINE DIRECT BLUE EB, E3B, ANTHRAQUINONE BLUE, ANTHRACYANINE, ERIOCYANINE LM, FAST SKY BLUE, BRILLIANT ANTHRAZUROL, ALIZARINE EMERALDOL G, ACID ALIZARINE GREEN G.
	Bright yellow, orange, or orange-brown	On the addition of a few drops of dilute caustic soda (1 : 20), no change occurs.	18.	ALIZARINE DIRECT BLUE B, ALIZARINE CYANOL B, ALIZARINE ASTROL, ALIZARINE URANOL, ALIZARINE SKY BLUE, ALIZARINE CARMINE BLUE, CYANANTHROL, ALIZARINE IRISOL, ALIZARINE CYANOL VIOLET, ALIZARINE DIRECT VIOLET, ANTHRAQUINONE VIOLET, ALIZARINE GERANOL, ALIZARINE RUBINOL, ALIZARINE CYANINE GREEN, ALIZARINE BRILLIANT GREEN, ALIZARINE DIRECT GREEN, ALIZARINE VIRIDINE, BRILLIANT ALIZARINE VIRIDINE, ANTHRAQUINONE GREEN, ANTHRAQUINONE BLUE GREEN, MONOCHROME GREEN.
		On the addition o a few drops of dilute caustic soda (1 : 20), the colour becomes more intense, and bluer	19.	ALIZARINE RED (S MARKS), ERWECO ALIZARINE ACID RED, ALIZARINE ORANGE SW, ALIZARINE CYANINE, BRILLIANT ALIZARINE CYANINE, ANTHRACENE BLUE (S MARKS), ACID ALIZARINE BLUE, ALIZARINE DARK GREEN W, ALIZARINE BLUE (S MARKS), ALIZARINE GREEN S, ALIZARINE BLACK S, ALIZARINE INDIGO BLUE (S MARKS), CŒRULEINE (S MARKS).

TABLE VII.—DYESTUFFS INSOLUBLE IN WATER:

Sulphide, Mordant, Pigment, Spirit Soluble, and Vat Dyestuffs.

<table>
<tr><td colspan="9">Add a small quantity of the dyestuff to 5 per cent. caustic soda, and warm.</td></tr>
<tr><td colspan="3">The dyestuff dissolves. Add a little zinc-dust and ammonia to the alkaline solution, and boil.</td><td colspan="6">The dyestuff is insoluble in caustic soda. Boil with 95 per cent. alcohol.</td></tr>
<tr><td colspan="2">Solution is decolourised, or changed in shade to yellow-brown or brown. On pouring on to filter-paper, original colour returns. Apply stannous chloride and lead acetate test.</td><td rowspan="3">Solution is decolourised. On pouring on to filter-paper, original colour does not return: Mordant Dyes of the Nitroso and Azo Classes.</td><td colspan="3">The dyestuff dissolves in 95 per cent. alcohol. Reduce the alcoholic solution with zinc-dust and acetic acid.</td><td colspan="3">The dyestuff is insoluble in 95 per cent. alcohol. Apply stannous chloride and lead acetate test.</td></tr>
<tr><td rowspan="2">A brown stain is produced: Sulphide Class.</td><td rowspan="2">No stain is produced: Mordant Dyes of the Anthracene, Pyrone, and Oxazine Classes.</td><td rowspan="2">Colour remains unchanged: Quinoline Class.</td><td rowspan="2">Decolourised, but colour returns in air or on spotting with acid permanganate: Azine and Triphenylmethane Classes.</td><td rowspan="2">Permanently decolourised: Nitro and Azo Classes.</td><td rowspan="2">A brown stain is produced: Sulphur Vat Colours.</td><td colspan="2">No brown stain is produced. Reduce with caustic soda (1 per cent.) and hydrosulphite. The dyestuff dissolves: Vat Dyestuff.</td></tr>
<tr><td>The leuco compound is yellow or clear orange: Indigoid Class.</td><td>The leuco compound is dark coloured: Anthracene and Naphthacene Classes.</td></tr>
<tr><td>1.</td><td>2.</td><td>3.</td><td>4.</td><td>5.</td><td>6.</td><td>7.</td><td>8.</td><td>9.</td></tr>
<tr><td>INSOLUBLE SULPHIDE COLOURS OF THE AURANOL, CROSS-DYE, ECLIPSE, IMMEDIAL, KATIGEN, KRYOGENE, PYROGENE, PYROL, SULPHUR, THIOGENE, THION, THIONAL, THIONOL, AND THIOXINE SERIES.</td><td>ALIZARINE, ANTHRAPURPURINE, FLAVOPURPURINE, PURPURINE, RESOFLAVINE, GALLOFLAVINE, ALIZARINE BLACK, ALIZARINE BROWN, ANTHRACENE BROWN, ANTHRAGALLOL, ALIZARINE GARNET, ALIZARINE MAROON, ALIZARINE BLUE, ANTHRACENE BLUE, ALIZARINE CYANINE, ALIZARINE BORDEAUX, BRILLIANT ALIZARINE BORDEAUX, ALIZARINE CYANINE BLACK, GALLAMINE BLUE, GALLOCYANINE, ALIZARINE GREEN, CŒRULEINE, GALLEINE.</td><td>ALIZARINE YELLOW 2G, R, ANTHRACENE YELLOW 2G, RUSSIAN GREEN, GAMBINE, FAST PRINTING GREEN, ALSACE GREEN, RESORCIN GREEN, DIOXINE, FAST GREEN O, VIRIDONE FF.</td><td>QUINOLINE YELLOW (SPIRIT SOL.).</td><td>NIGROSINE (SPIRIT SOL.), INDULINE (SPIRIT SOL.), MELASINE, OIL BLACK, SPIRIT BLACK, SPIRIT BLUE, OLEATE GREEN.</td><td>SUDANS, BUTTER YELLOW, CERASINE ORANGE, OIL YELLOW, OIL ORANGE, TUSCALINE ORANGE, PIGMENT CHLORIN, LITHOL FAST YELLOW, PIGMENT CHROME YELLOW, CERASINE RED, LITHOL FAST ORANGE, LITHOL FAST SCARLET, AUTOL REDS, HELIO FAST RED, HANSA YELLOW, HANSA RED, LAKE REDS, SITARA FAST RED, PIGMENT ORANGE, PIGMENT RED, PIGMENT CLARET, PERMANENT REDS, PIGMENT PURPLE, OIL SCARLET, OIL RED, OIL VERMILION.</td><td>HYDRON BLUE, HYDRON BROWN, HYDRON DARK BLUE, HYDRON OLIVE, HYDRON VIOLET, CIBANONE BLACK, CIBANONE BLUE, CIBANONE BROWN, CIBANONE GREEN, CIBANONE OLIVE, INDANTHRENE OLIVE, ALGOL BROWN B, ALGOL OLIVE, ALGOL DARK GREEN, LEUCOL BROWN, LEUCOL DARK GREEN, HELINDONE BLACK, HELINDONE ORANGE D. HELINDONE BLUE 3R, INDOCARBON BLACK.</td><td>VAT COLOURS OF THE CIBA, HELINDONE, AND THIOINDIGO SERIES. INDIGO, BROMINDIGO, BRILLIANT INDIGOS, ALIZARINE INDIGO, ALIZARINE INDIGO RED, ALIZARINE INDIGO GREY, ALGOL SCARLET, THIOINDONE GREEN, VAT RED.</td><td>VAT COLOURS OF THE ALGOL AND INDANTHRENE SERIES. CIBANONE ORANGE, ANTHRAFLAVONE, HELINDONE FAST SCARLET C, HELINDONE ORANGE GRN, HELINDONE BLACK G, 2RG, HELINDONE YELLOW RN, HELINDONE BROWN AN, CR, CIBA INDIGO YELLOW 3G, CIBA YELLOW G, 2R, 5R, CIBA RED R, CIBA SCARLET G, CIBA BROWN R, LEUCOL BROWN B, LEUCOL DARK GREEN B, LEUCOL YELLOW G, THIOINDIGO SCARLET 2G, SIRIUS YELLOW, HELIO FAST YELLOWS, HELIO FAST PINK.</td></tr>
</table>

CHAPTER V.

THE IDENTIFICATION OF DYESTUFFS ON ANIMAL FIBRES.

THE ready identification, by an examination of a textile material, of the dyestuff or dyestuffs with which it has been dyed or printed is a problem which at the present day is associated with great difficulties. Twenty-five or thirty years ago the number of dyestuffs was so small that their identification by an expert was a simple enough matter, for the shade alone would usually give a sufficient indication. With the enormous increase both in individual colouring-matters and in new groups of colouring-matters, their detection has been rendered both more necessary and greatly more difficult, since it is now possible to produce any shade in a large variety of ways. The fact that the fastness of such a shade for the purpose in view will depend upon a suitable choice of the dyestuff or dyestuffs renders it particularly important for the dyer, in matching a sample submitted, to be able not only to match the shade, but, if necessary, to select the same or similar dyestuffs. It is also a desideratum for the merchant to be able to ascertain whether the colour of the material dyed for him is always of constant composition, whether the shade dyed by one firm is or is not a chemical match for that dyed by another, and other similar problems. Although an extensive series of tables have been published by Schultz, Lange, Knecht and Löwenthal, Rawson, Lunge, Gnehm, Heermann, and others, giving the reactions towards acids, alkalies, etc., of the individual dyestuffs on the fibre, there is yet required a systematic analytical scheme without which such tables are of little use. A scheme of this kind should be capable of referring the dyestuff to its chemical group; after which the particular brand may, if necessary, be ascertained by comparing the individual reactions with the published tables. In very many cases, however, sufficient information for the practical dyer would be gained by knowing the group to which the dyestuff belongs.

Whilst we may limit ourselves in the commencement to the consideration of single dyestuffs (or mixtures of dyestuffs of the same class), yet it is an absolute essential for any scheme of analysis that it should be capable of extension to all the mixtures which may be encountered in practice. For this reason, only those chemical properties can be employed as group reactions which depend upon general differences in chemical structure rather than upon individual peculiarities, so that dyestuffs of the same family shall be grouped together irrespective of shade. Another reason why this principle alone can prove satisfactory is, that the scheme must be capable of referring to their respective chemical and dyeing groups the many new colouring-matters which are constantly appearing and whose individual reactions are still unknown.

As already explained in Chapters II. and III., dyestuffs may be classified in two ways: either according to their dyeing properties, viz., whether "basic," "acid," "salt," "mordant," "vat," etc.; or according to their chemical structure, that is, according to the chromophor they contain, *e.g.*, whether they belong to the nitro, nitroso, azo, triphenylmethane, azine, oxazine, thiazine, acridine, pyrone, anthracene, or other groups. In the scheme of analysis here presented, use is made, in the first place, of tests for ascertaining the dyeing property of the dyestuff on the fibre, such tests (so-called "stripping tests") being an inversion of the respective dyeing process. In the second place, in order to ascertain the chemical relationship of the dyestuff, there is employed a modification of the method described in Chapter IV. for the analysis of dyestuffs in substance, and which depends upon the difference in their behaviour when submitted to reduction and reoxidation. Whilst nitro, nitroso, and azo compounds are completely destroyed on reduction, those dyestuffs which may be regarded as having an *ortho* quinonoid structure give leuco compounds which are readily oxidised by air to the original dyestuff, and those to which a *para* quinonoid structure is attributable give leuco compounds stable to air, but reoxidised by acidified permanganate or chromic acid. A still further group of dyestuffs is very resistant to reduction, whilst those of the anthraquinone class are distinguished by giving *coloured* leuco compounds.

These reactions can be satisfactorily performed upon the wool or silk fibre if sodium hydrosulphite is used as the reducing agent in place of zinc-dust, whilst potassium persulphate is employed in place of permanganate as the oxidising agent. Contrary to what might have been anticipated, the leuco compounds formed remain in great part attached to the fibre, whilst the splitting products of the azo dyestuffs can be entirely removed therefrom by washing. The reactions are therefore in many cases sharper than when carried out in substance, as there is no disturbing factor due to secondary oxidation products.

The following is the general behaviour of the various chemical classes of dyestuffs upon animal fibres towards reduction and oxidation:—

Decolourised by Hydrosulphite.			Not altered by hydrosulphite.	Not decolourised, but changed in shade. Original colour restored by air or by persulphate.
Colour restored on exposure to air.	Colour not restored by air, but on oxidation with persulphate.	Colour not restored either by air or by persulphate.		
AZINES, OXAZINES, THIAZINES, INDIGOIDS.	TRIPHENYL-METHANE GROUP.	NITRO, NITROSO, AND AZO GROUPS.	PYRONE, ACRIDINE, QUINOLINE, AND THIAZOL GROUPS. SOME MEMBERS OF ANTHRACENE GROUP	MOST DYESTUFFS OF THE ANTHRACENE GROUP.

Having ascertained both the dyeing character and the chemical relationship of the colouring-matter, and taking the shade also into consideration, the question is usually narrowed down to a single representative or to a choice between a few closely related dyestuffs. In order to distinguish between these the behaviour with concentrated sulphuric acid, strong hydrochloric acid, or caustic soda can be employed. For final confirmation it is well to compare the sample both as to shade and reactions with a dyed pattern of the dyestuff to which it is believed to correspond. In the appended tables the subdivision of the groups has, owing to exigencies of space, being usually omitted. For the same reason the list of individual dyestuffs mentioned under each division is of necessity incomplete, only typical members being given. These lists must therefore only be regarded as a guide and not as a complete enumeration of all colouring-matters belonging to the respective groups.

It should be remarked that the same degree of definiteness cannot be expected as in a system of inorganic analysis, and some variation will be found in the sharpness of the indications with individuals of the same class. A little practice and experience therefore will be required before absolute certainty can be obtained. It may also be pointed out that whilst many commercial dyestuffs are single chemical compounds, others are not infrequently mixtures, sometimes even comprising members of two different groups. Thus, some of the brands of direct cotton blues are mixtures of "acid" dyestuffs of the triphenyl-methane class with "salt" dyestuffs of the disazo class. Such mixtures will therefore exhibit the reactions of both classes.

In the appended tables all the possible groups of dyestuffs are considered, although in individual instances many of them would be at once excluded on account of the nature of the material or its shade. In such cases, therefore, the analytical scheme may be much simplified.

Reagents. — The following reagents are employed. It is important that they should be used of the strength indicated:—

Dilute Ammonia (1 : 100).—1 c.c. concentrated ammonia to 100 c.c. water (soft or distilled).

Aqueous Alcoholic Ammonia.—1 c.c. concentrated ammonia to 50 c.c. strong alcohol or methylated spirit and 50 c.c. water.

Dilute Acetic Acid (5 *per cent.*).—5 c.c. glacial acetic acid to 95 c.c. water.

Dilute Alcohol (1 : 1). — 50 c.c. strong alcohol or methylated spirit to 50 c.c. water.

Dilute Hydrochloric Acid (1 : 10).—10 c.c. concentrated hydrochloric acid to 100 c.c. water.

Caustic Soda (10 *per cent.*).—10 grams solid caustic soda in 100 c.c. of solution.

Hydrosulphite B.—50 grams of Hydrosulphite NF concentrated (Meister), Hyraldite C extra (Cassella), or Rongalite C (Badische), *i.e.* the formaldehyde compound of sodium sulphoxylate, dissolved in 500 c.c. of water and acidified with 2 c.c. of acetic acid. Only used for yellow and orange colours.

Hydrosulphite AX. — Dissolve 50 grams of Hydrosulphite NF concentrated or Rongalite C in 150 c.c. of hot water. Add to the hot solution (at 80° or 90° C.) ¼ gram of anthraquinone (precipitated not sublimed) which has been previously ground to a fine paste with a little of the solution, and dilute the whole to 500 c.c. with cold water. The solution should always be slightly alkaline to litmus paper. It may become acid on keeping.

Persulphate.—A cold saturated solution of potassium persulphate, or a 1 per cent. solution of ammonium persulphate. If the solution is alkaline it should be carefully neutralised with dilute acid.

Sodium Acetate (*5 per cent.*). — 5 grams crystallised sodium acetate in 100 c.c. water.

Procedure.—*General.*—The reactions are performed in test-tubes with pieces of the material about ½ to ¾ in. (12–18 mm.) square, which are covered to 1 to 1½ in. (25–35 mm.) deep with the reagent. The tests should be carried out exactly as described. Except when specially stated, the reagents are to be applied in succession to fresh portions of the material. In making "stripping tests" the degree of stripping is judged by comparing the depth of shade remaining against that of the original pattern: the colour of the stripping solution is misleading and can scarcely be relied upon as a guide. When a fabric is composed of two or more differently coloured threads, these should be removed and tested separately. It is found advantageous in boiling with dilute acetic acid and dilute ammonia to repeat the extraction, as a better stripping is thereby obtained, and any staining of the white cotton by acid dyestuffs which may occur on the first extraction is removed by the second. In testing with dilute ammonia or sodium acetate, the material is placed in a test-tube with a somewhat smaller piece of white *mercerised* cotton cloth, and boiled for the time prescribed. If the shade is a pale one, the size of the sample should be increased and that of the cotton diminished. The dilute ammonia is replaced by aqueous alcoholic ammonia in the case of the violet and black dyestuffs (Tables X. and XIV.), as in these cases the acid dyestuffs are less easily extracted. On boiling with sodium acetate solution, white cotton is appreciably stained by salt dyestuffs after *one* minute; by salt-mordant colours after *two* minutes. In making reduction tests, the sample is boiled for from one-quarter to one minute with the hydrosulphite, then rinsed *thoroughly* under the tap and allowed to lie on white paper for an hour or so. With most dyestuffs which form air-oxidisable leuco compounds, the colour returns immediately or in a few minutes. The reaction is accelerated by exposing the pattern to ammonia vapour. If the colour does not return, the pattern is heated to boiling in a test-tube with a little water, and potassium persulphate is added drop by drop, carefully avoiding an excess. If this also fails to cause any return of colour, the dyestuff is to be regarded as an azo, nitro, or nitroso compound. The depth of the restored colour varies greatly in different cases; whilst with some dyestuffs the colour reappears with nearly its original depth, with others (probably on account of the greater solubility of their leuco compounds) the restored shade is much paler. Safranine and its azo derivatives yield on reoxidation of the leuco compound a violet colour. This is due to the condensation of the leuco-safranine with the formaldehyde present in the Hydrosulphite NF.

Doubt may sometimes arise as to how a particular shade should be classified, whether, for instance, a reddish blue is to be regarded as a blue or as a violet. In such cases the tables referring to both colours should be consulted: this can scarcely give rise to confusion since the same general scheme is employed throughout the tables. The same remark applies to possible mixtures; thus, in examining a green shade, not only the green table, but also the blue and yellow tables may be required.

The reactions given in the analytical scheme have special reference to the wool fibre, but with slight variations in some cases will apply also to silk.

For reactions distinguishing individual dyestuffs of the same group the reader is referred to the *Farbstofftabellen*, by G. Schultz (5. Aufl.), and to Heermann's *Koloristische und Textilchemische Untersuchungen.* For additional confirmation it is well to compare the sample both as to shade and reactions with a dyed pattern of the colouring-matter to which it is believed to correspond.

Preliminary Tests.—Before commencing the systematic examination it is advisable to ascertain, by boiling the pattern in plain distilled water, whether it contains unfixed dyestuffs, or finishing materials, which, if present, should be removed. It is also recommended to make a rapid provisional test for metallic mordants, which is conducted as follows:—

A few fibres are burnt in the Bunsen flame. If any ash is left, its colour is observed and its behaviour on ignition.

Al: White ash, incandescent when heated.

Sn: White ash, yellow and very incandescent when heated.

Cr: Greyish-green ash, yellow borax bead.

Fe: Reddish-brown ash.

In drawing deductions from any of the above indications it should be borne in mind that metallic oxides may be present which have no relationship to the dyestuff, as, for instance, chromium oxide in stripped shoddy wool and stannic oxide in weighted silk.

Tests for Acid and Salt Dyestuffs.—The difference between these two classes is rather a gradual than an absolute one. Accordingly, it is sometimes difficult to decide whether a sample belongs to one or the other group. Most of the typical "salt" dyestuffs stain cotton strongly when boiled either in dilute ammonia or sodium acetate solution, but a few (such as the Sulphon colours) only stain feebly and upon prolonged boiling. On the other hand, whilst most acid dyestuffs do not stain cotton from boiling dilute ammonia, there are one or two which exhibit this property to some extent (such as Fast Red A and Wool Red B).

The stripping of acid colours on boiling with dilute ammonia also varies considerably in degree. Thus, whilst most acid dyestuffs lose much colour under the conditions employed, a few, such as Milling Yellow and some of the brands of Patent Blue, are stripped with difficulty.

Test for Indigoid Dyestuffs.—The pattern is boiled for a minute or two with aniline (freshly distilled), and the extract, if coloured, is carefully evaporated to dryness in a test-tube. The quite dry residue (free from aniline) is then carefully heated in a small Bunsen flame: the presence of an indigoid dyestuff is indicated by the production of coloured vapours. For distinguishing between the individual dyestuffs of the indigoid class, as, for instance, between Indigo and Ciba Blue, the colour of the chloroform extract, as recommended by Holden, is useful.

Confirmatory Test for Triphenylmethane Colours.—Most triphenylmethane colours become pale yellow or yellowish brown on treatment of the fibre with concentrated sulphuric acid.

Detection of Mordants.—In addition to the preliminary tests already mentioned, the following methods are recommended:—

Burn a small pattern of the material and fuse the ash with potassium or sodium chlorate, on a crucible lid (a yellowish-coloured mass indicates chromium), and allow to cool. To test for **Al** and **Cr**, add acetic acid in excess (tin and iron left insoluble, tin as white solid, iron as brown), filter and divide filtrate into two parts:—

(*a*) Test for chromate by lead acetate.

(*b*) Test for Al by adding ammonia in slight excess, together with a drop of very dilute alizarine paste. This, if Al is present, gives a red, flocculent precipitate, which is readily seen.

To test for Fe, Cu, and Sn, add HCl in excess to the product of fusion (or to the residue insoluble in acetic acid):—

(*c*) Fe gives a yellow solution and a blood-red colouration on addition of a sulphocyanide.

(*d*) Cu gives a brown colouration with sulphocyanide, and a blue solution on adding ammonia.

(*e*) Sn, on addition of ammonium sulphide, gives a brown precipitate.

Copper is usually not present in sufficient quantity to give the above test, but may be readily detected even in traces by the production of a green flame when the ash moistened with concentrated HCl is brought into the Bunsen flame.

The detection of the mordant (Cu or Cr) requires special care in those cases in which the dyestuff as sold already contains the mordant incorporated with it.

In the case of textile materials containing copper (used, for instance, for rendering acid colours faster to light), it is advisable to remove the copper by boiling with oxalic acid before proceeding to test for the dyestuff.

Mixtures.—Although it is not possible to lay down exact details of procedure in dealing with mixtures, a few general principles may be mentioned which will be found useful by those who wish to extend the scheme to such cases. If a mixture consists of two or more dyestuffs of the same chemical and dyeing group, it will behave as a whole similarly to a single dyestuff, though sufficient differences will usually exist in the rate of solution or of attack by the group reagents to render it possible to distinguish or even to separate the constituents. Thus, a green dyed by means of an Acid Azo Yellow and an Acid Azo Blue will be distinguishable upon careful reduction with hydrosulphite, since the Azo Blue will generally be reduced first, and the shade will therefore change from green to yellow before it is decolourised. Further, if such a compound shade be extracted fractionally with dilute ammonia, the yellow is generally stripped first, and after acidification may be transferred from the solution to another piece of wool for subsequent tests. Mixtures of colours belonging to different groups will usually exhibit at once their divers composition. For example, a navy blue shade dyed with Patent Blue and an Azo Orange will, upon reduction, first change to bright blue, then become colourless, and upon reoxidation with persulphate the blue alone will return. If a mixture of an azine, oxazine, or thiazine dyestuff with a triphenylmethane colour has been employed, only the first colour will return upon exposure of the leuco compound to air, the latter colour being restored also upon treatment with persulphate. Fractional extraction of the fibre with dilute alcohol or dilute acetic acid can be employed in many cases to effect a separation or partial separation of the dyestuffs present, the extracted colour being then transferred to fresh wool or silk and separately tested. To affect this transference the alcohol must be first boiled off or the acetic acid neutralised.

In some cases mixtures may be separated by means of solvents. Thus a mixture of a "mordant" colouring-matter fixed by chromium and an ordinary "acid" dyestuff may be resolved by extracting the pattern in a Soxhlet extracting apparatus with pyridine, which removes the "acid" dyestuff, leaving the "mordant" dyestuff in great part upon the fibre. After distilling off the pyridine from the extract, the residual colour can be dyed upon wool and tested. In order to separate indigo and other "vat" dyestuffs from "mordant" and "acid" dyestuffs, the solvent action of cresol (commercial cresylic acid 98 per cent.) upon the colours of the former class may be made use of. For this purpose it is advisable to reduce the boiling-point of the solvent by mixing it with a hydrocarbon of lower boiling-point. Thus a mixture of 100 parts of cresol with 30 parts of "solvent naphtha" (crude xylol) or of petroleum spirit of boiling-point 120° to 140° has been found suitable. The previously dried pattern is put in the Soxhlet apparatus, covered with a layer of loose wool, and a thermometer placed with its bulb in contact with the pattern. The proportion of hydrocarbon to cresol is so adjusted that the temperature of the extracting liquid is 100° to 105°. By this means the "vat" dyestuffs are extracted, but most of the "acid" and "mordant" dyestuffs remain on the fibre and can be subsequently examined. The method is used with advantage for the analysis of reputed indigo-dyed cloths, for further details of which see page 90.

Mixed shades obtained with logwood (hæmatein) and an "acid," "mordant," or "vat" dyestuff are easily separated by boiling with dilute hydrochloric acid, which removes the logwood, giving a crimson solution, whilst the other dyestuff (usually) remains upon the fibre. Brazil wood and other natural dye-woods behave similarly to logwood, whilst "acid" Alizarine Reds are also extracted. It is possible in some cases, as, for example, with a "vatted black" (mixture of indigo and logwood), to either remove the indigo by extraction with cresol or pyridine, leaving the logwood on the fibre, or to remove the logwood by boiling with dilute acid and leave the indigo. If in addition to these two dyestuffs an "acid" black, for instance, were also present, the logwood could be first removed by dilute acid, then the indigo by extraction with cresol, thus leaving the "acid" black alone upon the fibre.

Although the identification of dyestuffs employed in dyeing mixed shades must always be attended with some difficulty, experience and familiarity with the properties of the dyestuffs render it possible in a large number of cases to effect a successful analysis, and the instances given above will serve as a sufficient illustration of the methods of attacking the problem.

Notes on the Analytical Tables.

TABLE VIII.

General.—In the case of yellow and orange colours the indications are sharper when reduction is effected with Hydrosulphite B. With Hydrosulphite AX many of the dyestuffs of the thiazol group become considerably lighter, whilst, on the other hand, the decolourisation of the dyestuffs of other groups may be somewhat obscured by the yellow tint given by the anthraquinone, especially if the pattern is not thoroughly washed.

Div. 1.—The acridine dyestuffs give a more or less pronounced green fluorescence to the acetic acid extract.

Div. 6.—Turmeric becomes much browner on boiling with dilute ammonia or sodium acetate.

Div. 8.—Nitro dyestuffs may be distinguished from azo by the production with hydrosulphite, prior to decolourisation, of a reddish-orange colouration (nitroamido compound).

Div. 11.—Weld on **Al** is partially stripped by acetic acid, giving a colourless extract; on **Cr** or **Sn** it is not affected.

Div. 15.—Alizarine Yellow R and RW stain cotton slightly on boiling with sodium acetate solution.

Div. 17.—Sulphone Yellow and Sulphone Orange give only a comparatively slight stain on cotton after boiling two minutes with sodium acetate. The Toluylene Oranges are only reduced by hydrosulphite with great difficulty.

TABLE IX

Div. 2.—Induline Scarlet gives a claret-red colour with concentrated sulphuric acid, which becomes green on addition of a trace of water. Saffranine, after reduction and oxidation, does not return to its original shade, but to a violet (methylene derivative), which is reconverted into the red on boiling with ammonia.

Div. 9.—Fast Acid Red A, although a pyrone derivative, also falls into this division. It reduces more slowly than the triphenylmethane dyestuffs and is similar to the Fast Acid Violets of Table X.

Div. 10.—Fast Red A and Wool Red B stain cotton on boiling with dilute ammonia. The group of acid azo colours may be split up into classes by treatment of the fibre with concentrated sulphuric acid, when various colours are obtained (red, violet, blue, or green).

Div. 12.—Alizarine Geranol B exhibits an exceptional behaviour, being reduced by Hydrosulphite AX to a pale yellow, which is permanent in air but changed on boiling with persulphate to a pale violet-brown.

Div. 15.—Many of the red "vat" dyes show a yellow fluorescence in chloroform solution.

Div. 17.—Several of the red azo "mordant" dyestuffs, which should fall into this group, are, when fixed upon wool, extremely difficult to reduce. This is especially the case with Eriochrome Red B, Acid Alizarine Red G, Acid Alizarine Garnet R, Omega Chrome Red B, and Diamond Red G.

TABLE X.

Div. 1.—Cresyl Fast Violet 2B returns in air to a greenish blue instead of to a violet. Its acetic acid extract has a strong red fluorescence. Brilliant Rhoduline Violet R is a Rhodamine and comes into Table IX.

Div. 7.—The dyestuffs of the pyrone group reduce much more slowly than those of the triphenylmethane series. Violamine 3B falls into Table XI.

Div. 8.—Acid Violet 7B gives a bright green spot with concentrated hydrochloric acid.

Div. 13.—The indigoid "vat" colours only return slowly in air and usually through green (except Ciba Heliotrope).

Div. 14.—Chrome Violet (old) gives coloured extracts both with dilute acetic acid and with dilute ammonia, but the fibre is not markedly stripped.

TABLE XI.

Div. 1.—Certain "basic mordant" dyestuffs belonging to Div. 17 (Celestine Blue B, Correine 2R, Gallocyanine, etc.) tend to strip slightly with boiling 5 per cent. acetic acid.

Div. 8.—Certain brands of Wool Blue are mixtures containing Patent Blue.

Div. 9.—All the dyestuffs of the Patent Blue class are somewhat difficult to strip with dilute ammonia, some of the new marks being barely affected.

Div. 10.—The redder brands of the Chlorazol Brilliant Blues, Isamine Blues, Brilliant Dianil Blues, and Brilliant Sky Blues, are mixtures of the pure dyestuff represented by the bluest marks (triphenylmethane compounds) with a disazo dyestuff of Div. 25.

Div. 13.—The Cyananthrols and Alizarine Sky Blues are restored by persulphate to a slate grey instead of to the original blue. These dyestuffs are probably mixtures.

Div. 18.—Many of the Blues and Navy Blues of the Eriochrome series are mixtures, apparently of Eriochrome Azurol or of Eriochrome Cyanine with "mordant" azo dyestuffs. Eriochrome Blue S, B, and BR are azo mordant colours, as is also Eriochrome Dark Blue B.

Div. 19.—Helindone Grey and Thioindigo Grey fall into this group.

Div. 21.—Chrome Blue A is a mixture of a Chromotrope with a little Patent Blue. Chrome Blue B is also a mixture.

Div. 25.—The Sulphoncyanines and Sulphonazurines only stain cotton in sodium acetate solution upon long boiling. Brilliant Sulphonazurine is reduced by Hydrosulphite to a pink, which is only decolourised with great difficulty.

TABLE XII.

General.—As green shades are frequently produced with mixtures of blue and yellow dyestuffs, Tables VIII. and XI. should also be consulted.

Div. 5.—Brilliant Milling Green S is a dyestuff of the Patent Blue class, and on account of its shade would fall into Table XI.

Div. 8.—Anthracyanine Greens 3GL and BL, though mixtures, fall into this group.

Div. 13.—Eriochrome Olive, upon treatment with concentrated HCl, gives a crimson solution and fibre.

TABLE XIII.

General.—Brown shades are very frequently dyed with mixtures of dyestuffs, *e.g.* with an orange shaded with a blue or violet, for which colours the respective tables must be consulted. The commercial brown dyestuffs are also frequently mixtures.

Div. 1.—Diazine Brown might be classed as a violet.

Div. 3.—Anthracyanine Browns GL and RL, which are mixtures, fall into this group. On reduction with Hydrosulphite AX and oxidation with persulphate, a blue or grey-blue is obtained. Fast Brown G gives a rose-coloured strip with dilute ammonia.

Div. 4.—The "vat" colours after reduction return in air much less rapidly than do the stilbenes. Helindone Brown CR in particular returns very slowly, and should be confirmed by solubility in aniline. Ciba Brown R, unlike the other vat Browns, does not reduce to a pale yellow but to a yellowish brown.

Div. 7.—A number of "mordant" azo Browns appear to stain cotton very slightly on long boiling with sodium acetate solution.

TABLE VIII.—YELLOW AND ORANGE COLOURS.

<table>
<tr><td colspan="18">Boil twice for one minute with 5 per cent. acetic acid.</td></tr>
<tr><td colspan="5">Much colour is stripped: Basic Dyestuff. Boil with Hydrosulphite AX or B.</td><td colspan="13">Little or no colour is stripped: Acid, Vat, Mordant, or Salt Dyestuff. Boil twice for one minute with dilute ammonia (1 : 100) and a piece of white cotton. Keep the ammoniacal extract.</td></tr>
<tr><td colspan="4">Not decolourised, or only slightly altered. Treat fibre with cold conc. sulphuric acid.</td><td rowspan="4">De-colourised. Colour is not restored either by air or by persulphate: Azo Class.</td><td colspan="5">Much colour is stripped, but cotton remains white: Acid Dyestuff. Boil with Hydrosulphite AX or B.</td><td colspan="8">Little or no colour is stripped: Vat, Mordant, or Salt Dyestuff. Boil with Hydrosulphite AX or B.</td></tr>
<tr><td rowspan="3">Green fluorescent solution Acridine Class.</td><td colspan="3">Colourless solution: Ketonimide and Thiazol Class. Boil fibre with dilute hydrochloric acid (1 : 10).</td><td rowspan="3">Colour unaffected: Quinoline or Pyrone Class.</td><td colspan="4">Decolourised. Colour is not restored either by air or by persulphate: Azo or Nitro Class. Add excess of conc. hydrochloric acid to the ammoniacal extract.</td><td colspan="2">Colour unaffected, or only slightly changed in shade. Test for a mordant.</td><td colspan="2">Decolourised. Colour returns on exposure to air, or more quickly on oxidation with persulphate. Boil with 5 per cent. sodium acetate and a piece of white cotton for two minutes.</td><td colspan="3">Decolourised. Colour is not restored either by air or by persulphate: Azo Class. Test for a mordant (Cr).</td><td rowspan="3">Colour changed to yellow-brown or brown: Alizarine Class. A mordant is present.</td></tr>
<tr><td rowspan="2">Fibre and solution colourless.</td><td rowspan="2">Fibre and solution pale yellow.</td><td rowspan="2">Fibre and solution orange.</td><td rowspan="2">Colour unaffected.</td><td rowspan="2">Solution becomes colourless or very pale yellow.</td><td rowspan="2">Solution becomes red or orange-red.</td><td rowspan="2">Solution becomes violet or violet-red.</td><td rowspan="2">Mordant present: Flavone or Ketone Class.</td><td rowspan="2">Mordant absent: Thiazol Salt Dyestuff. Confirm by boiling with 5 per cent. sodium acetate and a piece of white cotton. The latter is stained.</td><td rowspan="2">Cotton remains white: Indigoid Vat Dyestuff. Confirm by extraction with aniline and sublimation test</td><td rowspan="2">Cotton is stained: Salt Dyestuff Stilbene Class.</td><td colspan="2">Mordant present Boil with 5 per cent. sodium acetate and a piece of white cotton for two minutes.</td><td rowspan="2">Mordant absent: Azo Salt Dyestuff. Confirm by boiling with 5 per cent. sodium acetate and a piece of white cotton. Stained.</td></tr>
<tr><td>Cotton remains white: Acid-mordant Dyestuff.</td><td>Cotton is stained: Salt-mordant Dyestuff.</td></tr>
<tr><td>1.</td><td>2.</td><td>3.</td><td>4.</td><td>5.</td><td>6.</td><td>7.</td><td>8.</td><td>9.</td><td>10.</td><td>11.</td><td>12.</td><td>13.</td><td>14.</td><td>15.</td><td>16.</td><td>17.</td><td>18.</td></tr>
<tr><td>PHOSPHINE, BENZOFLAVINE, CORIPHOSPHINE, RHEONINE, PATENT PHOSPHINE, ACRIDINE ORANGE, ACRIDINE YELLOW, FLAVOPHOSPHINE, AUROPHOSPHINE, DIAMOND PHOSPHINE, BRILLIANT PHOSPHINE, ETC.</td><td>AURAMINE.</td><td>THIOFLAVINE T, METHYLENE YELLOW H, RHODULINE YELLOW.</td><td>RHODULINE ORANGE N.</td><td>CHRYSOIDINE, TANNIN ORANGE, JANUS YELLOW, AZO PHOSPHINE, NEW PHOSPHINE, ETC.</td><td>QUINOLINE YELLOW, QUINALDINE YELLOW, URANINE, EOSINE ORANGE, ETC. ALSO TURMERIC.</td><td>ORANGE G, 2G, GT, R, ETC. CROCEINE ORANGE, TARTRAZINE, FLAVAZINE, HYDRAZINE YELLOW, FAST LIGHT YELLOW AND ORANGE, FAST WOOL YELLOW, WOOL FAST ORANGE, GUINEA FAST YELLOW, XYLENE YELLOW AND LIGHT YELLOW, TARTRAPHENINE, KITONE YELLOW, SUPRAMINE YELLOW, FAST ACID ORANGE RH, ETC.</td><td>NAPHTHOL YELLOW S, MARTIUS YELLOW, NAPHTHYLAMINE YELLOW, NAPHTHALENE YELLOW, CITRONINE A, ETC.</td><td>INDIAN YELLOW, FAST YELLOW, AZO FLAVINE, BRILLIANT YELLOW S, CURCUMINE, ORANGE II., PALATINE LIGHT YELLOW, WOOL FAST YELLOW, AZO ACID YELLOW, AZO YELLOW, ETC.</td><td>METANIL YELLOW, VICTORIA YELLOW, ORANGE IV., ORANGE MN, MNO, N, ETC.</td><td>FUSTIC, QUERCITRON BARK, WELD, FLAVINE, ALIZARINE YELLOW A AND C, GALLOFLAVINE, ETC.</td><td>THIOFLAVINE S, DIAMINE FAST YELLOW B, FF, M, SULPHINE, PRIMULINE, CHLORAMINE YELLOW, BRILLIANT PURE YELLOW, CHLORAZOL FAST YELLOW, THIAZOL YELLOW, CLAYTON YELLOW, CHLOROPHENINE, DIANIL PURE YELLOW HS, NAPHTHAMINE PURE YELLOW G, DIPHENYL FAST YELLOW, TRIAZOL FAST YELLOW, COLUMBIA YELLOW, OXYDIANIL YELLOW, OXYDIAMINE YELLOW, MIMOSA YELLOW, ETC.</td><td>HELINDONE YELLOW AND ORANGE, CIBA YELLOW AND ORANGE, CIBA INDIGO YELLOW 3G, THIOINDIGO YELLOW AND ORANGE, ETC.</td><td>CURCUMINE S, MIKADO YELLOW, GOLDEN YELLOW AND ORANGE, DIRECT YELLOW, STILBENE YELLOW, DIAMINE FAST YELLOW A, AR, DIAMINE ORANGE D, DIANIL DIRECT YELLOW S, CHLORAMINE ORANGE, NAPHTHAMINE YELLOW, DIPHENYL CHRYSOINE, DIPHENYL CITRONINE, SUN YELLOW, POLAR YELLOW, POLYPHENOL YELLOW, ETC.</td><td>ACID ALIZARINE YELLOW, ERIOCHROME YELLOW, ERIOCHROME PHOSPHINE, ALIZARINE YELLOW G, 2G, 3G, R, FLAVAZOL, DIAMOND FLAVINE, ANTHRACENE YELLOW, ALIZADINE YELLOW, CHROME FAST YELLOW, FAST MORDANT YELLOW, SALICINE YELLOW D, DIAMOND YELLOW, CHROME YELLOW, CHROME ORANGE, ETC.</td><td>AUTOCHROME ORANGE, MERCEROL YELLOW 2R, MERCEROL ORANGE 2R, SALICINE ORANGE G, SALICINE YELLOW G, METACHROME YELLOW, ETC.</td><td>CHRYSOPHENINE, CHRYSAMINE, DIAMINE FAST YELLOW 3G, DIAMINE YELLOW N, BENZO FAST YELLOW AND ORANGE, CONGO ORANGE, COTTON YELLOW, CARBAZOL YELLOW, PLUTO ORANGE, CRESOTINE YELLOW, PYRAMINE ORANGE, TOLUYLENE YELLOW AND ORANGE, ORANGE TA, HESSIAN YELLOW, DIANIL ORANGE, TRIAZOL YELLOW G, SULPHON YELLOW AND ORANGE, ETC.</td><td>ALIZARINE RED S, ETC., ON SN, ALIZARINE ORANGE SW ON CR, AL, SN.</td></tr>
</table>

TABLE IX.—RED COLOURS.

Boil twice for one minute with 5 per cent. acetic acid.																			
Much colour is stripped: **Basic Dyestuff or Soluble Red Wood.** Boil twice for one minute with dilute alcohol (1 : 1).						Little or no colour is stripped: **Acid, Vat, Mordant, or Salt Dyestuff.** Boil twice for one minute with dilute ammonia (1 : 100) and a piece of white cotton.													
Much colour is stripped: **Basic Dyestuff.** Boil with Hydrosulphite AX.					Unaffected. Al or Cr is present in ash. On boiling with dilute ammonia the colour becomes much bluer.	Much colour is stripped, but cotton remains white: **Acid Dyestuff.** Boil with Hydrosulphite AX.						Part of the colour is stripped, and the wool becomes bluer. Boil with Hydrosulphite AX.		Little or no colour is stripped: **Vat, Mordant, or Salt Dyestuff.** Boil with Hydrosulphite AX.					
Colour unaffected: **Pyrone Class.**	Decolourised. Colour returns on exposure to air. Treat original fibre with cold conc. sulphuric acid.		Decolourised. Colour does not return on exposure to air, but is restored by persulphate: **Triphenylmethane Class.**	Decolourised. Colour is not restored either by air or by persulphate: **Azo Class.**		Colour unaffected: **Pyrone Class.** On acidifying the ammoniacal extract, fluorescence is not discharged	Decolourised. Colour returns on exposure to air: **Azine Class.**	Decolourised. Colour does not return on exposure to air, but is restored by persulphate: **Triphenylmethane Class.**	Decolourised. Colour is not restored either by air or by persulphate: **Azo Class.** Boil with dilute bichromate.		Colour is changed to bright yellow, which slowly returns in air to original shade: **Anthraquinone Class.**	Colour unaffected: **Pyrone Class.** The ammoniacal extract is fluorescent, and on acidifying, the fluorescence is discharged.	Colour is changed to yellow. Original colour is not restored on exposure to air. Sn is present.	Decolourised Colour returns on exposure to air: **Indigoid Vat Dyestuff.** Confirm by extraction with aniline and sublimation test.	Decolourised Colour does not return on exposure to air, but is restored by persulphate. A mordant is present (Al or Cr).	Decolourised. Colour is not restored either by air or by persulphate: **Azo Class.** Test for a mordant (Cr).			Colour slowly changed to orange or orange-brown. Original colour is restored by persulphate A mordant is present **Alizarine Class.**
	Fibre and solution green: **Azine Class.**	Fibre and solution violet.							Colour unaffected.	Colour changed to dark maroon or blue-violet.						Mordant present Boil with 5 per cent. sodium acetate and a small piece of white cotton for two or three minutes.		Mordant absent: **Salt Dyestuff.** Confirm by boiling with 5 per cent. sodium acetate and a piece of white cotton.	
																Cotton remains white: **Acid-mordant Dyestuff.**	Cotton is stained: **Salt-mordant Dyestuff.**		
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11	12.	13.	14.	15.	16.	17.	18.	19.	20.
RHODAMINES, IRISAMINE, ANISOLINE, ROSAZEINE, RHODULINE PINK, ETC.	SAFRANINE, INDULINE SCARLET, RHODULINE RED, DIAZINE RED, BRILLIANT RHODULINE RED, BRILLIANT RHODULINE VIOLET R, BRILLIANT SAFRANINE, ETC.	CUDBEAR, ARCHIL.	MAGENTA, FUCHSINE, DIAMOND MAGENTA, NEW MAGENTA, CERISE, ETC.	JANUS RED.	SOLUBLE RED WOODS, *e.g.*, BRAZILWOOD, LIMAWOOD, SAPANWOOD, PEACHWOOD, ETC.	AN ACID EOSINE OR ACID RHODAMINE, *e.g.*, FAST ACID EOSINE, FAST ACID PHLOXINE, ACID RHODAMINE, ACID ROSAMINE, XYLENE RED, BRILLIANT KITONE RED, SULPHO ROSAZEINE, ETC.	ROSINDULINE, AZO CARMINE.	ACID MAGENTA, ACID FUCHSINE, FAST ACID RED A.	PALATINE SCARLET, XYLIDINE PONCEAU, VICTORIA SCARLET, LANAFUCHSINE, SORBINE RED, BIEBRICH ACID RED, CRYSTAL SCARLET, FAST RED, CROCEINE SCARLET, BIEBRICH SCARLET, WOOL AND CLOTH REDS, WOOL SCARLET, ACETYL RED, AMIDO NAPHTHOL RED, ERIOCARMINE, ERIORUBINE, AZO ACID RED, GUINEA FAST RED, FAST ACID COCHINEAL, ETC.	CHROMOTROPE, AZOFUCHSINE.	ALIZARINE RUBINOL.	EOSINE, EOSINE SCARLET, PHLOXINE, ERYTHROSINE, ROSE BENGALE, ETC.	COCHINEAL SCARLET.	HELINDONE RED, SCARLET, FAST SCARLET AND PINK, CIBA RED AND SCARLET, THIOINDIGO RED, THIOINDIGO SCARLET, VAT RED, ETC.	INSOLUBLE RED WOODS, *e.g.*, BARWOOD, CAMWOOD.	ANTHRACENE CHROME RED, ACID ALIZARINE RED, ERIOCHROME RED, ERIOCHROME BORDEAUX, ERIOCHROME GARNET, OXYCHROME GARNET, DIAMOND RED, PALATINE CHROME RED, OMEGA CHROME RED, ETC.	ANTHRACENE RED, ACID ANTHRACENE RED, AUTOCHROME RED, SALICINE RED, CHROME FAST RED, ETC.	DIAMINE, BENZO, DIANIL, CHLORAZOL, NAPHTHAMINE, ETC., REDS, SCARLETS, AND FAST SCARLETS, ERIKA, GERANINE, BENZOPURPURINE, MILLING REDS AND SCARLETS, POLAR RED, ETC.	ALIZARINE RED W, IWS, S, SB, PS, ETC., ERWECO ALIZARINE ACID RED SB.

TABLE X.—PURPLE AND VIOLET COLOURS.

Boil twice for one minute with 5 per cent. acetic acid.																	
Much colour is stripped: **Basic Dyestuff** or **Soluble Red Wood.** Boil twice for one minute with dilute alcohol (1 : 1).			Little or no colour is stripped: **Acid, Vat, Mordant,** or **Salt Dyestuff.** Boil twice for one minute with aqueous alcoholic ammonia (1 : 100) and a piece of white cotton.														
			Much colour is stripped, but cotton remains white: **Acid Dyestuff.** Boil with Hydrosulphite AX.							Little or no colour is stripped: **Vat, Mordant,** or **Salt Dyestuff.** Boil with Hydrosulphite AX.							
Much colour is stripped: **Basic Dyestuff.** Boil with Hydrosulphite AX.		Unaffected. Al or Cr is present in ash. On boiling with dilute ammonia, the colour becomes much bluer.	De-colourised. Colour returns on exposure to air: **Azine, Oxazine,** or **Thiazine Class.**	Decolourised. Colour does not return on exposure to air, but is restored by persulphate: **Triphenylmethane** and **Pyrone Classes.** Boil with 5 per cent. sodium acetate for one minute.				Decolourised. Colour is not restored either by air or by persulphate: **Azo Class.**	Colour is changed to orange-yellow, restored by persulphate to a violet-brown: **Anthraquinone Class.**	Colour unaffected: **Pyrone Class.** A chrome mordant is present.	Decolourised. Colour returns on exposure to air. Test for a mordant		Decolourised. Colour does not return on exposure to air, but is restored by persulphate: **Triphenylmethane Class.** A chrome mordant is present	Decolourised. Colour is not restored either by air or by persulphate: **Azo Class.** Test for a mordant (Cr).		Colour changed to orange-brown or brown: **Alizarine Class.** A mordant is present. Boil original fibre with dilute hydrochloric acid (1 : 10).	
Decolourised. Colour returns on exposure to air: **Azine, Oxazine,** or **Thiazine Class.**	Decolourised. Colour does not return on exposure to air, but is restored by persulphate: **Triphenylmethane Class.**			Much colour is stripped, but solution remains colour ess. Treat original fibre with cold conc. sulphuric acid.		Little colour is stripped Spot original fibre with conc. hydrochloric acid					Mordant present: **Azine, Oxazine,** or **Thiazine Class.**	Mordant absent: **Indigoid Vat Dyestuff.** Confirm by extraction with aniline and sublimation.		Mordant present: **Acid-mordant Dyestuff.**	Mordant absent: **Salt Dyestuff.** Confirm by boiling with 5 per cent. sodium acetate and a piece of white cotton. Stained.	Fibre and solution orange.	Fibre and solution red-brown to violet-brown
				Colour of fibre yellow to orange.	Fibre becomes reddish-brown.	Fibre unchanged.	Yellow spot.										
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13	14.	15.	16.	17.	18.
NEUTRAL VIOLET, RHODULINE VIOLET, RHODULINE HELIOTROPE, ROSOLANE, METHYLENE VIOLET, METHYLENE HELIOTROPE, TANNIN HELIOTROPE, IRIS VIOLET, ETC.	METHYL VIOLET, ETHYL VIOLET, CRYSTAL VIOLET, BENZYL VIOLET, BRILLIANT VIOLET, ETC.	SOLUBLE RED WOODS, *e.g.*, BRAZILWOOD, LIMAWOOD, SAPANWOOD, PEACHWOOD, ETC.	FAST BLUE R, RED SHADE INDULINES, ETC.	CERTAIN RED-SHADE ACID VIOLETS, *e.g.*, ACID VIOLET 4RS AND 5RS, RED VIOLET 4RS, ETC.	RED-SHADE SOLUBLE BLUES.	PYRONE COLOURS, *e.g.*, FAST ACID VIOLETS, VIOLAMINES, ACID VIOLET 4R, ETC.	ACID VIOLETS, ALKALI VIOLET, GUINEA VIOLET, FORMYL VIOLET, KITONE VIOLET, ETC.	LANACYL VIOLET, AZO ACID VIOLET, INDO VIOLET, SULPHON VIOLET, VICTORIA VIOLET, ERIO FAST PURPLE, WOOL VIOLET.	ANTHRAQUINONE VIOLET, ALIZARINE DIRECT VIOLET, ALIZARINE IRISOL, ALIZARINE CYANOL VIOLET, ERWECO ALIZARINE ACID BLUE.	GALLEINE.	GALLOCYANINE, PRUNE, CELESTINE BLUE, CORREINE.	HELINDONE VIOLET, CIBA VIOLET, CIBA HELIOTROPE, THIOINDIGO VIOLET, ETC.	CHROMOGENE VIOLET, METACHROME VIOLET, CHROME VIOLET.	ACID ALIZARINE VIOLET, ACID CHROME VIOLET, ERIOCHROME VIOLET, PALATINE CHROME VIOLET, OXYCHROME VIOLET.	DIAMINE, BENZO, DIANIL, COLUMBIA, CHLORAZOL, NAPHTHAMINE, CHLORANTINE, ETC., VIOLETS.	ALIZARINE RED S, ETC., ON Fe.	ALIZARINE BORDEAUX, ALIZARINE CLARET, ALIZARINE MAROON.

TABLE XI.—BLUE COLOURS.

Boil twice for one minute with 5 per cent acetic acid																									
Much colour is stripped **Basic Dyestuff** or **Logwood.** Boil with dilute alcohol (1 : 1) twice for one minute				Little or no colour is stripped: **Acid, Vat, Mordant, or Salt Dyestuff.** Boil twice for one minute with dilute ammonia (1 : 100) and a piece of white cotton. Keep the ammoniacal extract.																					
Much colour is stripped **Basic Dyestuff.** Boil with Hydrosulphite AX			Unaffected. Al or Cr is present in ash. On spotting with hydrochloric acid, the blue is changed to brick red	Much colour is stripped, but cotton remains white. **Acid Dyestuff.** Boil with Hydrosulphite AX									Little or no colour is stripped. **Vat, Mordant, or Salt Dyestuff.** Boil with Hydrosulphite AX												
Decolourised. Colour returns on exposure to air. **Azine, Oxazine, or Thiazine Class.**	Decolourised. Colour does not return on exposure to air, but is restored by persulphate. **Triphenylmethane Class.**	Decolourised. A violet colour returns on exposure to air. **Safranine Azo Dyestuff.**		Decolourised. Colour returns on exposure to air: **Azine, Oxazine, Thiazine, and Indigo Classes. Also Prussian Blue.**			Decolourised. Colour does not return on exposure to air, but is restored by persulphate. **Triphenylmethane Class.**			Decolourised. Colour is not restored either by air or by persulphate. **Azo Class.**	Fibre is not decolourised, but colour changes. **Anthraquinone Class.** Colour of reduced fibre is-		Colour unaffected, or slightly darker. **Anthraquinone Class.** Test for a mordant (Cr).		Decolourised. Colour returns on exposure to air. Test for a mordant.					Decolourised. Colour does not return on exposure to air, but is restored by persulphate. **Triphenylmethane Class.** Test for a mordant.		Decolourised. Colour is not restored either by air or by persulphate. **Azo Class.** Test for a mordant.			Colour changed to brown, becoming blue again on exposure to air. **Alizarine Class.** Mordant present.
				The ammoniacal extract is blue. On adding caustic soda		The ammoniacal extract is colourless. Fe is present in ash.	Ammoniacal extract is blue. Treat fibre with cold conc. sulphuric acid.		Ammoniacal extract is colourless, but becomes blue on acidifying		red-violet, returning with persulphate	bright yellow to orange brown, returning with persulphate	Mordant present	Mordant absent	Mordant present. **Azine, Oxazine, or Thiazine Class.** Treat fibre with cold conc. sulphuric acid			Mordant absent. Treat fibre with aniline		Mordant present	Mordant absent	Mordant present. Boil with 5 per cent sodium acetate and a piece of white cotton for two or three minutes		Mordant absent. **Salt Dyestuff.** Confirm by boiling with per cent sodium acetate and a piece of white cotton. Cotton stained.	
				at once becomes yellow	becomes violet on heating		Fibre and solution red brown to orange brown	Fibre and solution colourless to pale yellow							Fibre and solution green	Fibre and solution blue or violet	Fibre and solution red	Blue solution giving on evaporation a sublimable residue. **Indigoid Vat Dyestuff.**	Colourless solution. **Pyrone Dyestuff.**			Cotton remains white: **Acid-mordant Dyestuff.**	Cotton is stained. **Salt-mordant Dyestuff.**		
1	2.	3.	4.	5.	6.	7.	8.	9	10	11	12	13	14.	15.	16.	17	18	19.	20	21.	22.	23.	24.	25.	26
METHYLENE BLUE, NILE BLUE, CAPRI BLUE, CRESYL BLUE, MELDOLA'S BLUE NEW METHYLENE BLUE, DIPHENE BLUE, ETC.	NIGHT BLUE, VICTORIA BLUE, SETOCYANINE, SETOGLAUCINE, TURQUOISE BLUE, ETC	JANUS BLUE, DIAZINE BLUE, INDOINE BLUE, JANUS DARK BLUE, NAPHTHINDONE, ETC.	LOGWOOD BLUE.	INDIGO EXTRACT, INDIGO CARMINE.	THIOCARMINE, FAST BLUE, INDULINE, ACID CYANINE, FLUORESCENT BLUE, LAZULINE BLUE, ETC.	PRUSSIAN BLUE.	WOOL BLUE, CYANOLE FF, INTENSIVE BLUE, ETC.	PATENT BLUE, NEW PATENT BLUE, NEPTUNE BLUE, XYLENE BLUE, BRILLIANT ACID BLUE KITONE BLUE, ERIOGLAUCINE, ERIOCYANINE, ERIOCHLORINE, CYANOLE, CYANINE, FAST ACID VIOLET 10B, CYANOGENE, ETC.	SOLUBLE BLUE, WATER BLUE ALKALI BLUE, CHLORAZOL BRILLIANT BLUE 14B, ISAMINE BLUE 8B, BETAMINE BLUE 8B, BRILLIANT DIANIL BLUE 6G, BRILLIANT SKY BLUE 8G, DIRECT BLUE 12B, ETC	LANACYL BLUE, AZO ACID BLUE, AZO MERINO BLUE, AZO NAVY BLUE, CHROMAZONE BLUE, AZOCYANINE, ORTHOCYANINE, ETC.	ALIZARINE SAPHIROL, ANTHRACYANINE, ALIZARINE DIRECT BLUE EB AND E3B, ALIZARINE CYANOL EF, BRILLIANT ANTHRAZUROL, ERIOCYANINE LM, FAST SKY BLUE, ETC.	ALIZARINE ASTROL, ALIZARINE URANOL, CYANANTHROL, ALIZARINE DIRECT BLUE B, ALIZARINE CYANOL B, ALIZARINE SKY BLUE, ANTHRAQUINONE BLUE, ETC.	ALIZARINE CYANINE, BRILLIANT ALIZARINE CYANINE, ANTHRACENE BLUE, ALIZARINE INDIGO BLUE, ACID ALIZARINE BLUE 2B AND GR ETC.	INDANTHRENE BLUE WB.	BRILLIANT ALIZARINE BLUE, MERCEROL BRILLIANT BLUE, INDOCHROMINE, ETC.	GALLOCYANINE, CELESTINE BLUE, CORREINE, PRUNE, GALLAMINE BLUE, DELPHINE BLUE, BRILLIANT DELPHINE BLUE, INDALIZARINE, LANOGLAUCINE, ULTRA CYANINE, ULTRA VIOLET ETC	ERIOCHROME AZUROL, ERIOCHROME CYANINE, CHROME WORSTED BLUE, CHROMAL BLUE, CHROMOXANE BLUE, ETC	INDIGO, HELINDONE BLUE 3G AND 2B, CIBA BLUE, THIOINDIGO BLUE, ETC.	FAST ACID BLUE R, VIOLAMINE 3B.	CHROME BLUE.	BRILLIANT MILLING BLUE B.	CYPRUS BLUE, CHROMOTROPE BLUE, ACID CHROME BLUE, CHROME FAST BLUE, ANTHRACENE CHROME BLUE, FAST MORDANT BLUE, SALICINE CHROME BLUE, MONOCHROME BLUE, ETC	AUTOCHROME BLUE.	DIAMINE, BENZO DIANIL CHICAGO CHLORAZOL, NAPHTHAMINE ETC BLUES AND SKY BLUES. SULPHON ACID BLUE SULPHONCYANINE SULPHONAZURINE ERIO FAST BLUE SWR. TOLYL BLUE GR EXTRA AND 5R EXTRA, ETC	ALIZARINE BLUE (ANTHRAQUINOLINE CLASS).

TABLE XII.—GREEN COLOURS.

<table>
<tr><td colspan="18">Boil twice for one minute with 5 per cent. acetic acid.</td></tr>
<tr><td colspan="3" rowspan="2">Much colour is stripped: Basic Dyestuff. Boil with Hydrosulphite AX.</td><td colspan="15">Little or no colour is stripped: Acid, Vat, Mordant, or Salt Dyestuff. Boil twice for one minute with dilute ammonia (1 : 100) and a piece of white cotton.</td></tr>
<tr><td colspan="5">Much colour is stripped, but cotton remains white: Acid Dyestuff. Boil with Hydrosulphite AX.</td><td colspan="10">Little or no colour is stripped: Vat, Mordant, or Salt Dyestuff. Boil with Hydrosulphite AX.</td></tr>
<tr><td rowspan="4">De-colourised. A dark violet colour returns on exposure to air: Safranine Azo Dyestuff.</td><td rowspan="4">Decolourised. Original colour returns on exposure to air: Azine, Oxazine, or Thiazine Class.</td><td rowspan="4">Decolourised. Colour does not return on exposure to air, but is restored by persulphate: Triphenyl-methane Class.</td><td rowspan="4">De-colourised. Colour returns on exposure to air: Azine, Oxazine, or Thiazine Class.</td><td rowspan="4">Decolourised. Colour does not return on exposure to air, but is restored by persulphate: Triphenyl-methane Class.</td><td rowspan="4">De-colourised. Colour is not restored either by air or by persulphate: Azo Class.</td><td colspan="2">Fibre is not decolourised, but colour changes: Anthraquinone Group. Colour of reduced fibre is—</td><td colspan="2">Decolourised. Colour returns on exposure to air. Test for a mordant.</td><td rowspan="4">Decolourised. Colour does not return on exposure to air, but is restored by persulphate: Triphenyl-methane Class. A Cr mordant is present.</td><td colspan="4">Decolourised. Colour is not restored either by air or by persulphate: Azo or Nitroso Class. Test for a mordant.</td><td rowspan="4">Colour changed to red-violet. The original colour is restored by persulphate. A chrome mordant is present.</td><td colspan="2">Colour changed to orange or orange-brown: Alizarine Class.</td></tr>
<tr><td rowspan="3">Red-violet returning with persulphate to bluish-green.</td><td rowspan="3">Orange, returning with persulphate to grey-green.</td><td rowspan="3">Mordant present: Oxazine or Thiazine Class.</td><td rowspan="3">Mordant absent: Indigoid Vat Dyestuff. Confirm by extraction with aniline and sublimation test.</td><td colspan="3">Mordant present. Boil with 5 per cent. sodium acetate and a piece of white cotton for two or three minutes.</td><td rowspan="3">Mordant absent: Salt Dyestuff. Confirm by boiling with 5 per cent. sodium acetate and a piece of white cotton.</td><td rowspan="3">Original colour returns on exposure to air. A mordant is present.</td><td rowspan="3">Original colour does not return on exposure to air, but is restored by persulphate. A chrome mordant is present.</td></tr>
<tr><td colspan="2">Cotton remains white. Boil original fibre with conc. hydrochloric acid.</td><td rowspan="2">Cotton is stained: Salt-mordant Dyestuff.</td></tr>
<tr><td>Fibre and solution light brown: Nitroso Class.</td><td>Colour of fibre unchanged, or bluer: Azo Class.</td></tr>
<tr><td>1.</td><td>2.</td><td>3.</td><td>4.</td><td>5.</td><td>6.</td><td>7.</td><td>8.</td><td>9.</td><td>10.</td><td>11.</td><td>12.</td><td>13.</td><td>14.</td><td>15.</td><td>16.</td><td>17.</td><td>18.</td></tr>
<tr><td>JANUS GREEN, DIAZINE GREEN.</td><td>METHYLENE GREEN, CAPRI GREEN, AZINE GREEN, FAST GREEN M, ETC.</td><td>MALACHITE GREEN, BRILLIANT GREEN, FAST GREEN, SETOGLAUCINE, SOLID GREEN, CHINA GREEN, NEW FAST GREEN, ETC.</td><td>AZINE GREEN S.</td><td>ACID GREEN, LIGHT GREEN, GUINEA GREEN, WOOL GREEN, NEPTUNE GREEN, NAPHTHALENE GREEN, ALKALI FAST GREEN, CYANOLE FAST GREEN, AGALMA GREEN, ERIOVIRIDINE, ERIO GREEN, BRILLIANT MILLING GREEN B, NIGHT GREEN, ETC.</td><td>SULPHON ACID GREEN, MIXTURES OF AN AZO BLUE AND YELLOW.</td><td>ALIZARINE EMERALDOL, ALIZARINE DIRECT GREEN.</td><td>ANTHRAQUINONE GREEN, ALIZARINE CYANINE GREEN, ALIZARINE BRILLIANT GREEN, FAST ACID GREEN RH, ANTHRAQUINONE BLUE-GREEN.</td><td>ALIZARINE GREEN B AND G.</td><td>CIBA GREEN G, HELINDONE GREEN G.</td><td>CHROMOXANE GREEN, CHROME GREEN, FAST CHROME GREEN, ETC.</td><td>NAPHTHOL GREEN B, GAMBINES, DIOXINE, CHROME GREEN G, ETC.</td><td>DIAMOND GREEN B AND 3G, CHROMOXAL GREEN, CYPRUS GREEN, OMEGA CHROME GREEN, ERIOCHROME GREEN H AND L, ACID CHROME GREEN, CHROME FAST GREEN, ETC.</td><td>DIAMOND GREEN 2S, CHROME PATENT GREEN N, MERCEROL GREEN, ETC.</td><td>DIAMINE, BENZO, DIANIL, COLUMBIA, CHLORAZOL, NAPHTHAMINE, ETC., GREENS.</td><td>ERIOCHROME VERDONE, ACID ALIZARINE GREEN.</td><td>CŒRULEINE, ALIZARINE GREEN S, ALIZARINE DARK GREEN W.</td><td>ALIZARINE CYANINE GREEN, ALIZARINE VIRIDINE, BRILLIANT ALIZARINE VIRIDINE, ETC.</td></tr>
</table>

TABLE XIV.—BLACK AND GREY COLOURS.

<table>
<tr><td colspan="11">Boil twice for one minute with 5 per cent acetic acid.</td></tr>
<tr><td rowspan="5">Much colour is stripped Basic Dyestuff.</td><td colspan="10">Little or no colour is stripped: Acid, Mordant, or Salt Dyestuff. Boil twice for one minute with aqueous alcoholic ammonia (1 100) and a piece of white cotton</td></tr>
<tr><td colspan="2">The colour is stripped Acid or Salt Dyestuff.</td><td colspan="8">Little or no colour is stripped: Mordant Dyestuff. Boil for half a minute with dilute hydrochloric acid (1 10)</td></tr>
<tr><td rowspan="3">The cotton remains white Acid Dyestuff. On boiling with Hydrosulphite AX the colour is permanently discharged</td><td rowspan="3">The cotton is stained Salt Dyestuff. On boiling with Hydrosulphite AX, the colour is permanently discharged</td><td rowspan="3">Fibre and solution crimson</td><td rowspan="3">Fibre and solution orange to pale brown</td><td rowspan="3">Fibre blue or blue violet, solution crimson Test for indigo by extraction, evaporation, and sublimation</td><td colspan="5">Fibre unaffected Boil with Hydrosulphite AX</td></tr>
<tr><td colspan="2">Unaffected. Treat original fibre with cold conc sulphuric acid</td><td colspan="2">The colour is discharged Boil for one minute with 5 per cent sodium acetate and a piece of white cotton</td><td rowspan="2">Colour changed to brown Original colour returns slowly on exposure to air</td></tr>
<tr><td>Blue solution</td><td>Colourless solution</td><td>Cotton remains white</td><td>Cotton is stained</td></tr>
<tr><td>1</td><td>2.</td><td>3</td><td>4.</td><td>5.</td><td>6.</td><td>7.</td><td>8.</td><td>9.</td><td>10</td><td>11</td></tr>
<tr><td>JANUS BLACK, DIAZINE BLACK, JUTE BLACK, METHYLENE GREY, NEW FAST GREY, ETC.</td><td>NAPHTHOL BLACK, NAPHTHYLAMINE BLACK, NEROL, AMIDO BLACK, AMINE BLACK, AZO ACID BLACK, AZO MERINO BLACK, PALATINE BLACK, SUPRAMINE BLACK, SULPHONCYANINE BLACK, SULPHON BLACK, BIEBRICH PATENT BLACK, CRESOL BLACK, GUINEA BLACK, ETC</td><td>UNION BLACK, COLUMBIA, DIAMINE, DIANIL, BENZO, CHLORAZOL, NAPHTHAMINE, ETC BLACKS AND FAST BLACKS, CARBIDE BLACK, DIRECT DEEP BLACK, DIRECT BLUE BLACK, CHROMANIL BLACK, COTTON BLACK ETC</td><td>LOGWOOD ON CR.</td><td>LOGWOOD ON FE, BONSOR'S BLACK.</td><td>A "VATTED BLACK" (INDIGO AND LOGWOOD)</td><td>ALIZARINE CYANINE BLACK.</td><td>ANILINE BLACK.</td><td>DIAMOND BLACK PV, PVB, P2B F, DIAMOND BLUE BLACK EB, ERIOCHROME BLACK, ERIOCHROME GREY, CHROME FAST BLACK, ANTHRACENE CHROME BLACK, ACID ALIZARINE BLACK, FAST CHROME BLACK, ACID CHROME BLACK ACID ALIZARINE GREY, AUTOCHROME GREY ETC</td><td>DIAMOND BLACK FB, FR, NG, GA, 2B, PALATINE CHROME BLACK, ANTHRACENE ACID BLACK, ALIZADINE BLACK, MONOCHROME GREY, ANTHRACENE CHROMATE GREY ETC</td><td>NAPHTHAZARINE, ALIZARINE BLUE BLACK SW, W BRILLIANT ALIZARINE BLACK ALIZARINE BLACK S WR, WX, ETC.</td></tr>
</table>

Div. 9.—Alizarine Brown G is a mordant azo dyestuff.

Div. 10.—Cutch in heavy shades is liable to be slightly stripped by Hydrosulphite AX becoming more orange.

TABLE XIV.

General.—The reduction of black colours with Hydrosulphite seldom gives rise to a pure white, the shade obtained usually having a brownish or greyish tint.

Divs. 9 *and* 10.—Many salt and mordant blacks bleed when boiled with dilute hydrochloric acid, giving blue or violet liquids, but the colour of the fibre is little altered.

CHAPTER VI.

THE IDENTIFICATION OF DYESTUFFS ON VEGETABLE FIBRES.

In the scheme for the analysis of colours on animal fibres described in the previous chapter, the dyeing properties of the colouring-matter present on the fibre, *i.e.* whether "acid," "basic," "mordant," "salt," etc., were determined by means of so-called "stripping" tests; whilst its chemical relationships were ascertained by its behaviour on reduction and reoxidation.

In applying the same principles to the analysis of colours on vegetable fibres (cotton), several initial difficulties are encountered, arising more especially from the influence exerted by mordants on the properties of the dyestuffs and the difference between the affinity of colouring-matters for the two types of fibre. Many "basic" dyestuffs, for instance, which if dyed on wool are easily reduced by sodium hydrosulphite, are scarcely attacked by this reagent when fixed on tannin-mordanted cotton. Nor can basic dyestuffs so fixed be stripped by acetic acid as they can from the wool fibre. Further, whilst in the case of wool the leuco compounds of dyestuffs remain in great part attached to the fibre, and can therefore be reoxidised, this is frequently not the case with cotton. It is necessary, moreover, to reckon with the fact that cotton dyes comprise a larger range of separate groups, some of which are not used in dyeing wool, and also that the analytical scheme must be applicable both to dyed and printed colours. The problem presented is therefore a more complicated one than the detection of colours on wool, and it is necessary to somewhat modify the system employed for the latter, though still retaining the same general principles. Owing to variations in properties between individual dyestuffs belonging to the same group, which are often great, and to the fact that many dyestuffs occupy a more or less intermediate position between two groups both in relation to chemical structure and to behaviour, it is not possible for any scheme of analysis to claim perfect mechanical accuracy, but much will always depend upon the skill and experience of the operator.

In adapting the analytical scheme to vegetable fibres (cotton) several points require special attention. Firstly, in order to overcome the difficulty introduced by the presence of a tannin mordant, it is necessary to remove the latter by boiling with caustic soda; and to avoid stripping the dyestuff at the same time, the reagent must be saturated with common salt. The "basic" dyestuffs are thus left on the fibre in the form of free colour-bases, which can then be readily stripped by boiling with dilute acetic or formic acid. Although most other colours are unaffected by boiling with the "saline caustic soda," as the above reagent is termed, some mordant dyes, such as Turkey Red, are partially decomposed. In such a case the acetic or formic acid extract will usually not have the colour of the dyed material, but in order to avoid any possibility of error from this cause, it is best, if the colour is appreciably stripped, to add to the acid extract a solution of tannin, when a coloured precipitate will result if a "basic" dyestuff is present.

As already mentioned, many "basic" dyestuffs fixed upon a tannin mordant do not give leuco compounds upon reduction with hydrosulphite, or if the leuco compound is formed, it may pass into solution and thus render reoxidation on the fibre impossible. To overcome this difficulty, the "basic" dyestuff is transferred to wool and the tests with hydrosulphite and persulphate are performed on this fibre instead of upon the original cotton (for procedure see Chapter V.). The transference of a "basic" colour from cotton to wool is very readily and quickly accomplished after the removal of the tannin mordant (method later). This procedure also affords the further advantage that in the case of pale shades the colour can be concentrated from a large piece of cotton on to a small piece of wool, and the tests thus rendered more distinct. Moreover, if the colour is a mixture, an opportunity is possibly offered of effecting a separation, since the different components may vary in their relative affinity for the two fibres.

Transference to wool before applying the hydrosulphite and oxidation tests is also adopted in the case of "acid" colours.

The "basic-mordant" dyestuffs (Gallocyanine, etc.), when treated with saline caustic soda, followed by dilute formic acid, behave like "basic" dyestuffs, except that they are less completely extracted. The acid extracts, though precipitated by tannin, give a finer and less distinct precipitate. As a means of distinction from ordinary "basic" dyestuffs, use is made of the fact that they are precipitated by chromium fluoride.

With dyestuffs not belonging to the "acid" or "basic" class, the reduction and oxidation tests must be performed on the cotton fibre itself, preferably before further differentiation. Certain azo colours, especially the insoluble azo compounds formed on the fibre, exhibit considerable resistance to reduction by the ordinary hydrosulphite solutions, and are decolourised very slowly and incompletely. To overcome this difficulty, use is made of the fact that the reducing power of hydrosulphites is greatly increased by the presence of very small quantities of certain colouring-matters or other reducible substances. The compounds which exert this effect in the most marked degree are Induline Scarlet, Alizarine, and Anthraquinone. Of these the last is the most suitable for the purpose, since it does not stain the cotton, and when added in small quantity to the hydrosulphite solution, slightly acidified with acetic acid, gives a reagent (termed "Hydrosulphite BX") which readily effects rapid and complete reduction in all cases.

It has hitherto not been found possible to devise any certain method of distinguishing between the "salt" colours which have received no after-treatment and those which have been subsequently "fixed" by development, by coupling with diazo compounds, or by treatment with formaldehyde, etc. In all these cases white cotton is stained more or less when boiled with the dyed material in a soap or sodium carbonate solution; and though the degree of staining is often much less with the "developed" or "fixed" colours than with the direct dyeings, and may after some practice be relied on as a means of differentiation in special cases, *e.g.* for Blacks, no absolute method can be based upon it. It is also obvious that since such developed colours do not differ chemically from the dyestuffs of the same composition prepared in substance and afterwards applied, no method of distinguishing between them by a chemical test can be expected. The difficulty is still further increased by the very large number of individual colouring-matters which the group of "salt" dyestuffs now comprises.

For the identification of "sulphide" colours the production of hydric sulphide upon boiling the fibre with stannous chloride is employed. As already mentioned, the indications of this test require to be accepted with some caution, as there are several possibilities of error due to the presence of other sulphur compounds giving rise to hydric sulphide upon reduction, such as albumen, bisulphite compounds, ultramarine, "antichlor," etc. It should also be noted that many "salt" dyestuffs evolve hydric sulphide when boiled with stannous chloride, apparently through reduction of sulphonic groups. It therefore becomes necessary to exclude the presence of "salt" dyestuffs before employing this test for "sulphide" colours.

In the tables which follow later there is given under each section a list of the chief dyestuffs it includes. Owing to the exigencies of space, and the large number of products now on the market, which are constantly augmented by new ones, these lists can only be regarded as a guide, and in no sense as a complete enumeration of all the colouring-matters belonging to the respective sections.

Reagents.—*Weak Ammonia* (1 : 100).—1 c.c. strong ammonia to 100 c.c. distilled water.

Dilute Caustic Soda.—10 grams caustic soda in 100 c.c. water.

Saline Caustic Soda.—10 c.c. caustic soda solution (35 to 40 per cent. NaOH) to 100 c.c. saturated solution of salt.

Formic Acid (90 *per cent.*).—Ordinary commercial strength.

Weak Formic Acid (1 : 100).—1 c.c. formic acid (90 per cent.) to 100 c.c. distilled water.

Dilute Hydrochloric Acid (1 : 20).—5 c.c. hydrochloric acid (30 per cent.) to 100 c.c. of water.

Soap Solution.—10 grams soap in 300 c.c. of water.

Tannin Solution.—10 grams tannin and 10 grams sodium acetate in 100 c.c. of water.

Bleaching Powder Solution.—Fresh solution at 5° Tw.

Hydrosulphite B.
Hydrosulphite AX. } See page 58.

Hydrosulphite BX.—Dissolve 50 grams of Rongalite or Hydrosulphite NF concentrated in 125 c.c. of hot water. Grind 1 gram of anthraquinone (precipitated not sublimed) to a fine powder, and reduce to a smooth paste with a little of the Rongalite solution. Add this paste to the remaining solution hot, and heat the whole for one or two minutes at about 90° C. Then dilute with cold water to 500 c.c., and after standing till cold add 1½ c.c. of glacial acetic acid. Keep in a well-stoppered bottle with greased stopper. The reagent should be tested occasionally by trying its effect on cotton dyed with Alphanaphthylamine Bordeaux, which should be fully discharged after boiling for one or two minutes.

Persulphate Solution.—A cold saturated solution of potassium persulphate, or a 1 per cent. solution of ammonium persulphate.

Acid Stannous Chloride.—100 grams stannous chloride to 100 c.c. hydrochloric acid (30 per cent.) and 50 c.c. water. The hydrochloric acid must be free from arsenic. In testing for "sulphide" colours this reagent may be replaced if desired by a strong solution of titanous chloride.

Chromium Fluoride Reagent.—A solution of 10 grams chromium fluoride and 5 grams sodium acetate in 100 c.c. of water.

Procedure.—*General.*—All the reactions are performed in test-tubes, usually with pieces of material about ½ to ¾ in. (12 to 18 mm.) square, which are just covered with the reagent. The degree of stripping is judged by comparing the depth of shade remaining against that of the original pattern; the colour of the stripping solution is misleading, and can scarcely be relied upon as a guide. In testing the colours of calico prints, the different shades should be cut out and the reactions tried upon them separately. With cotton and wool or cotton and silk unions the weft is separated from the cotton warp and both submitted to examination. Doubt may frequently arise as to how a particular shade should be classified, whether, for instance, a reddish blue is to be regarded as a blue or a violet. In such cases the tables referring to both colours should be employed; since the same general scheme is adopted throughout the tables, this can scarcely give rise to difficulty. The same remark applies to possible mixtures; thus in examining a certain green shade, both the yellow and the blue tables may require to be used. To distinguish between individual dyestuffs of the same group, the reactions towards concentrated sulphuric acid, caustic soda, etc., may be employed.[1] For additional confirmation it is well to compare the sample both as to shade and reactions with a dyed pattern of the colouring-matter or colouring-matters to which it is believed to correspond.

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[1] See G. Schultz, *Farbstofftabellen*, 5 Aufl.; P. Heermann, *Koloristische und Textilchemische Untersuchungen.*

It is obvious that in many instances the analytical procedure may be greatly simplified by exclusion of dyestuffs the presence of which is rendered improbable or impossible by the special circumstances of the case, *e.g.* by the material, shade, or mode of application.

Stripping Test for Acid Colours.—A few "salt" dyestuffs are partially stripped by weak ammonia, and may thus give rise to the impression that they are "acid" colours. To avoid this error it is advisable to add a small piece of white cotton when carrying out the test. If the dyestuff is an acid one the cotton is either not tinted or becomes white on boiling a second time with weak ammonia.

Transference of Basic Colours to Wool.—The tannin mordant is first removed, as in testing for a "basic" colour, by boiling the pattern for a quarter of a minute with saline caustic soda. It is then well washed with cold water (or, if the base is soluble, with salt solution) to remove all alkali, and is boiled with a piece of white wool (half the size of the cotton or less) in a little plain water for one or two minutes. In most cases the dye-base will leave the cotton almost entirely, and dye the wool a full shade. If the colour does not develop on the wool one or two drops of weak formic acid (1 : 100) may be added. In exceptional cases it may be necessary to extract the colour with dilute hydrochloric acid (1 : 20) carefully neutralising the extract with ammonia before adding the wool.

Transference of Acid Colours to Wool.—The cotton is simply boiled with a small piece of wool and weak formic acid (1 : 100).

Tannin Test for Basic Colours.—Add a few drops of tannin solution to the formic acid extract. Shake well, and if the precipitate does not form at once allow to stand a few minutes. Some colouring-matters, such as the Rhodamines, Gallocyanines, and Chrome colours of the Rosaniline series (which contain carboxyl or hydroxyl groups in addition to basic groups) only precipitate slowly, whilst the precipitate being more finely divided is sometimes difficult to see.

Bleeding Test for Salt Dyestuffs.—In testing for "salt" dyestuffs by the bleeding test, the sample is placed in a test-tube together with a smaller piece of white mercerised cotton cloth, and boiled with soap solution for about a minute. The soap solution may be replaced by a 5 per cent. solution of sodium carbonate.

Lead Acetate Test for Sulphide Colours.—The sample is just covered with Acid Stannous Chloride solution. The mouth of the test-tube is closed by a cap of filter-paper closely wrapped round it, into the centre of which is placed by means of a glass rod one drop of lead acetate solution. The contents of the test-tube are slowly heated to the boiling-point, when a blackish-brown stain of lead sulphide appears if a "sulphide" colour is present. The brown spot will again disappear on boiling the solution longer, owing to the decomposition of the lead sulphide by the hydrochloric acid evolved. In order to avoid the possibility of error through extraneous sulphur present on the cotton, the pattern should be previously boiled for half a minute with 10 per cent. caustic soda and then well boiled with water. It must, however, be borne in mind that the indications of the "sulphide" dyestuffs are rendered less sharp by this latter treatment. It is important to pay special attention to the cleanliness of the test-tubes employed for this test, as tubes which have been previously used for hydrosulphite reductions acquire a thin invisible deposit of sulphur upon their walls, which on boiling with stannous chloride gives rise to hydric sulphide and thus may lead to error. It is best to keep a special test-tube for this test alone.

Reduction and Reoxidation Tests.—The reduction with Hydrosulphite BX is carried out by boiling the sample with the reagent for from a minute to a minute and a half. The azines, thiazines, oxazines, etc., and most of the azo dyestuffs are fully reduced in about half a minute, but the insoluble azo colours and some salt dyestuffs require longer boiling to complete their reduction. In testing the reoxidisability by air, the reduced sample may be exposed to the fumes from an ammonia bottle, which in many cases accelerates oxidation.

Tests for Vat Dyestuffs.—For further particulars see Green and Frank, *Journal of the Society of Dyers and Colourists*, 1910, p. 83; also Grandmougin, *Tabellarische Uebersicht der Kupenfarbstoffe.*

TABLE XV.—YELLOW AND ORANGE COLOURS.

<table>
<tr><td colspan="18">Boil with weak ammonia (1 : 100).</td></tr>
<tr><td colspan="3">The colour is stripped. Boil with acidified water and small piece of white wool.</td><td colspan="15">The colour is not stripped. Boil for a quarter of a minute with saline caustic soda, rinse with cold water, and boil with water and one or two drops of weak formic acid (1 : 100).</td></tr>
<tr><td rowspan="5">Colour not transferred to the wool. Sn is present in ash.</td><td colspan="2">Colour is transferred to the wool : **Acid Dyestuff.** Boil wool with Hydrosulphite B.</td><td colspan="4">The colour is completely destroyed, both solutions and fibre being colourless. Treat original fibre with cold ammonium sulphide.</td><td colspan="3">The colour is completely or largely stripped, giving a coloured acid extract, which is precipitated by tannin solution : **Basic Dyestuff.** Transfer to wool and boil with Hydrosulphite B.</td><td colspan="8">A coloured acid extract precipitable by tannin is not obtained. Reduce original fibre with Hydrosulphite BX.</td></tr>
<tr><td rowspan="4">Not decolourised : **Pyrone or Quinoline Class.**</td><td rowspan="4">Permanently decolourised : **Azo Class.**</td><td rowspan="4">Fibre blackened, Cr present in ash.</td><td colspan="3">Fibre is not blackened, Boil with Hydrosulphite BX.</td><td colspan="2">Wool is not decolourised. Boil cotton with hydrochloric acid (1 : 20).</td><td rowspan="4">Wool is permanently decolourised : **Azo Class.**</td><td colspan="4">Decolourised or becomes light yellow. Original colour is not restored by air oxidation : **Azo Dyestuff** (including **the Stilbene Class**). Boil with soap solution and white mercerised cotton.</td><td colspan="4">The colour is unaffected or changed in shade, becoming lighter, browner, or bluer. If altered in shade, exposure to air restores the original colour. Apply the lead acetate test.</td></tr>
<tr><td colspan="2">Not decolourised. Test for Al in ash.</td><td rowspan="3">Decolourised.</td><td rowspan="3">Decolourised.</td><td rowspan="3">Not decolourised. The conc. H_2SO_4 and alcoholic solutions are fluorescent : **Acridine Class.**</td><td colspan="2">White cotton is stained : **Salt Dyestuff.**</td><td colspan="2">White cotton is not stained. Boil with pyridine</td><td rowspan="3">H_2S is evolved : **Sulphide Dyestuff.**</td><td colspan="3">No H_2S is evolved. Boil with soap solution and white mercerised cotton.</td></tr>
<tr><td rowspan="2">Al present.</td><td rowspan="2">Al absent.</td><td rowspan="2">Fibre after reduction is light yellow and can be diazotised and developed red with betanaphthol : **Primuline Azo Colour.**</td><td rowspan="2">Fibre after reduction is colourless : **Salt Azo Dyestuff.**</td><td rowspan="2">Colour is stripped : **Insoluble Azo Colour.**</td><td rowspan="2">Colour is not stripped Cr present in the ash : **Azo Mordant Dyestuff.**</td><td rowspan="2">The white cotton is stained : **Thiazol Salt Dyestuff.**</td><td colspan="2">The white cotton is not stained : **Mordant or Vat Dyestuff.** Boil with 90 per cent. formic acid. Also test ash for metallic mordant.</td></tr>
<tr><td>Colour stripped by formic acid. Al or Cr in ash : **Mordant Dyestuff.**</td><td>Colour not stripped by formic acid. No mordant in ash : **Vat Dyestuff.**</td></tr>
<tr><td>1.</td><td>2.</td><td>3.</td><td>4.</td><td>5.</td><td>6</td><td>7.</td><td>8.</td><td>9.</td><td>10.</td><td>11.</td><td>12.</td><td>13.</td><td>14.</td><td>15</td><td>16.</td><td>17.</td><td>18.</td></tr>
<tr><td>PERSIAN BERRIES ON TIN MORDANT.</td><td>QUINOLINE YELLOW, EOSINE ORANGE.</td><td>INDIAN YELLOW, ORANGE IV., G, ETC.</td><td>CHROME YELLOW OR CHROME ORANGE (LEAD CHROMATE).</td><td>ALIZARINE YELLOW A.</td><td>THIOFLAVINE T, METHYLENE YELLOW, RHODULINE YELLOW.</td><td>FLAVINDULINE.</td><td>AURAMINE.</td><td>PHOSPHINE, BENZOFLAVINE, ACRIDINE YELLOW, CORIPHOSPHINE, RHEONINE, PATENT PHOSPHINE, FLAVOPHOSPHINE, AUROPHOSPHINE, ACRIDINE ORANGE, ETC.</td><td>CHRYSOIDINE, TANNIN ORANGE, JANUS YELLOW, AZO PHOSPHINE, NEW PHOSPHINE, ETC.</td><td>PRIMULINE DEVELOPED WITH PHENOL OR WITH RESORCINOL, COTTON YELLOW G AND R, ORIOL YELLOW, DIANIL YELLOW, ETC.</td><td>CHRYSOPHENINE, CHRYSAMINE, CARBAZOL YELLOW, TOLUYLENE YELLOW AND ORANGE, STILBENE YELLOWS AND ORANGES, BENZO, CONGO, DIAMINE, AND DIANIL YELLOWS AND ORANGES, PYRAMINE ORANGE, PLUTO ORANGE, ETC.</td><td>METANITRANILINE ORANGE, NITROTOLUIDINE ORANGE, ORANGE FROM NAPHTHOL AC.</td><td>CHROME ORANGE, ALIZARINE YELLOW R, GG, ETC. DIAMOND FLAVINE, FLAVAZOL, ETC.</td><td>YELLOWS AND ORANGES OF THE IMMEDIAL, KATIGENE, CROSS-DYE, PYROGENE, THIOGENE, SULPHUR, THIONAL, ETC., SERIES.</td><td>CHLOROPHENINE, CHLORAMINE YELLOW, DIAMINE FAST YELLOW B, FF, AND C, CLAYTON YELLOW, THIAZOL YELLOW, THIOFLAVINE S, ETC. PRIMULINE DEVELOPED WITH HYPOCHLORITE.</td><td>PERSIAN BERRIES ON AL OR CR MORDANTS, ALIZARINE ORANGE ON AL MORDANT.</td><td>HELINDONE ORANGE R, HELINDONE YELLOW 3G, ANTHRAFLAVONE G, ALGOLE YELLOW 3G AND R, ALGOLE ORANGE R, INDANTHRENE YELLOW, INDANTHRENE ORANGE RT AND GOLDEN ORANGE, INDANTHRENE COPPER, CIBANONE YELLOW R AND ORANGE R.</td></tr>
</table>

TABLE XVI.—RED COLOURS.

Boil with weak ammonia (1 : 100).															
The colour is stripped: **Acid Dyestuff.** Transfer to wool and boil with Hydrosulphite AX.		The colour is not stripped. Boil for a quarter of a minute with saline caustic soda, rinse with cold water, and boil for one minute with water and one or two drops of weak formic acid (1 : 100).													
		The colour is completely or largely stripped, giving a coloured acid extract, which is precipitated by tannin solution: **Basic Dyestuff** (on tannin or other mordant). Transfer to wool and boil with Hydrosulphite AX.				A coloured acid extract precipitable by tannin is not obtained. Reduce original fibre with Hydrosulphite BX									
						Decolourised and colour not restored by air or by persulphate: **Azo Class.** Boil with soap solution and white mercerised cotton.				Becomes yellow or colourless. Colour returns on exposure to air: **Azine or Indigo Class.** Apply lead acetate test. Also heat fibre in dry tube.		Colour changed to greenish yellow (not restored to original colour by air), which can be diazotised and developed red with betanaphthol: **Primuline Azo Colour.**	Colour unaffected or changed to maroon or brown. Original colour restored on exposure to air: **Anthracene Class.** Boil with 90 per cent. formic acid. Also test ash for mordant.		
						The white cotton is stained: **Salt Dyestuff.** Test ash for Cr and Cu.		The white cotton is not stained. Boil with pyridine.						Colour but little affected by formic acid.	
Not decolourised: **Pyrone Class.**	Decolourised. Colour not restored by air or persulphate: **Azo Class.**	Wool not decolourised: **Pyrone Class.**	Wool decolourised. Colour returns on exposure to air: **Azine Class.**	Wool decolourised. Colour does not return on exposure to air, but is restored by persulphate: **Triphenylmethane Class.**	Wool decolourised. Colour not restored by air or by persulphate: **Azo Class.**	No Cr or Cu present: **Azo Salt Dyestuff.**	Cr or Cu present: **Azo Salt Dyestuff after-treated.**	The colour is stripped: **Insoluble Azo Colour.**	The colour is not stripped. Cr in ash: **Mordant Azo Dyestuff.**	H_2S is evolved **Sulphide Dyestuff.**	No H_2S is evolved. Red vapours on heating: **Indigoid Vat Dyestuff.**		Colour stripped by formic acid. Al in ash: **Anthracene Mordant Dyestuff.**	Cr in ash: **Anthracene Mordant Dyestuff.**	Cr absent **Anthracene Vat Dyestuff.**
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.
EOSINES, PHLOXINE, ERYTHROSINE, ROSE BENGAL, ETC.	CROCEIN SCARLETS, BRILLIANT CROCEINES, PALATINE SCARLET, FAST REDS, ETC.	RHODAMINES, RHODINES, IRISAMINE, ANISOLINE, ROSAZEIN, RHODULINE PINK, ACRIDINE REDS, ETC.	SAFRANINES, RHODULINE REDS AND PINK, AZINE SCARLET, INDULINE SCARLET, NEUTRAL RED, ETC.	MAGENTA, FUCHSINE, NEW FUCHSINE, ISORUBINE, CERISE, GRENADINE, ETC.	JANUS RED.	BENZOPURPURINE, DIAMINE SCARLETS, DIAMINE REDS, BENZO FAST SCARLETS, DIAZO BRILLIANT SCARLET, ROSANTHRENES, ZAMBESI RED, ERICA, DIAMINE ROSE, GERANINE, ROSOPHENINE, ETC.	DIAMINE FAST RED F, ETC.	PARANITRANILINE RED, ALPHANAPHTHYLAMINE BORDEAUX, CHLORANISIDINE PINK, NITROANISIDINE PINK, SCARLET AND REDS FROM NAPHTHOL AC.	CHROME RED, BRILLIANT CHROME RED, CHROME BORDEAUX, ETC.	THIOGENE RUBINE, ETC.	ALGOLE RED 5G AND SCARLET G, ALGOLE PINK R, CIBA RED G AND SCARLET G, CIBA BORDEAUX B, HELINDONE RED B AND 3B, HELINDONE SCARLET S, HELINDONE FAST SCARLET R, THIOINDIGO RED B, THIOINDIGO SCARLET, VAT RED.	PRIMULINE DEVELOPED WITH BETANAPHTHOL OR WITH R-SALT.	TURKEY RED, ALIZARINE RED, ALIZARINE PINK, ALIZARINE MAROON.	ALIZARINE, PURPURINES OR ALIZARINE MAROON ON CR MORDANT.	ALGOLE RED B, INDANTHRENE RED, INDANTHRENE CLARET, CIBA SCARLET G.

TABLE XVII.—PURPLE AND VIOLET COLOURS.

Boil with weak ammonia (1 : 100).																			
The colour is stripped: **Acid Dyestuff.** The colour transferred to wool is decolourised by Hydrosulphite A and restored by persulphate: **Triphenylmethane Class.**		The colour is not stripped. Boil for a quarter of a minute with saline caustic soda, rinse with cold water (or salt solution), and boil for one minute with water and one or two drops of weak formic acid (1 : 100).																	
		The colour is completely or largely stripped, giving a coloured acid extract, which is precipitated by tannin solution: **Basic Dyestuff** (on tannin or other mordant) or **Basic Mordant Dyestuff.** Add chromium fluoride reagent to the extract.						A coloured acid extract precipitable by tannin is not obtained. Reduce original fibre with Hydrosulphite BX.											
		Not precipitated: **Basic Dyestuff.** Transfer to wool and boil with Hydrosulphite AX.				Precipitated. Cr is present in ash: **Basic Mordant Dyestuff.** Boil cotton with Hydrosulphite BX.		Decolourised and colour not restored by air or persulphate: **Azo Class or Alizarine on Iron** (decolourised slowly). Boil with soap solution and white mercerised cotton.					Decolourised or yellowish. Colour restored on exposure to air: **Azine, Oxazine, Thiazine, or Indigoid Classes.** Apply lead acetate test. Also heat fibre in dry test-tube.			The colour is unaffected or only changed in shade, being restored to original on exposure to air: **Pyrone or Anthracene Class.** Test ash for mordant.			
								The white cotton is stained: **Salt Dyestuff.** Test ash for Cr and Cu.		The white cotton is not stained. Boil with hydrochloric acid (1 : 20).				No H_2S is evolved Test ash for mordant.		Al or Cr is present: **Mordant Dyestuff.**		Mordants are absent. Apply lead acetate test.	
											The colour is not stripped. Boil with pyridine.								
The ammoniacal solution is colourless, but becomes blue on acidifying.	The ammoniacal solution is violet.	Not decolourised: **Pyrone Class.**	Decolourised. Colour returns on exposure to air: **Azine (Oxazine or Thiazine) Class.**	Decolourised. Colour does not return in air, but is restored by persulphate: **Triphenylmethane Class.**	Decolourised. Colour is not restored by air or persulphate: **Azo Class.**	Decolourised. Colour returns on exposure to air: **Oxazine Class.**	Decolourised only slowly. Colour does not return in air, but is restored by persulphate: **Triphenylmethane Class.**	No Cr or Cu present: **Azo Salt Dyestuff.**	Cr or Cu present: **Azo Salt Dyestuff after-treated.**	Colour destroyed, giving yellow solution. Fe present in ash: **Alizarine Red on Fe Mordant.**	The colour is stripped. **Insoluble Azo Colour.**	The colour is not stripped Cr present in ash: **Mordant Azo Dyestuff.**	H_2S is evolved: **Sulphide Dyestuff.**	Cr is present. No coloured vapours on heating: **Mordant Oxazine Dyestuff** (not falling in group 7)	Cr is absent. Coloured vapours on heating: **Indigoid Dyestuff.**	The colour on reduction is unchanged.	The colour on reduction is browner or darker.	H_2S is evolved: **Sulphide Dyestuff.**	No H_2S is evolved: **Anthracene Vat Dyestuff.**
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.	17.	18.	19.	20.
RED SHADES OF SOLUBLE AND ALKALI BLUES.	ACID VIOLETS, FORMYL VIOLETS, ALKALI VIOLET, GUINEA VIOLET, ETC.	ANISOLINE.	METHYLENE VIOLET, RHODULINE VIOLET, IRIS VIOLET, NEUTRAL VIOLET, TANNIN HELIOTROPE, ETC.	METHYL VIOLETS, ETHYL VIOLET, BENZYL VIOLET, CRYSTAL VIOLET, ETC.	JANUS CLARET RED, ETC.	GALLOCYANINE, MODERN VIOLET, ULTRA VIOLET, COREINE, PRUNE, ETC.	CHROME VIOLET.	VIOLETS OF THE DIAMINE, BENZO, CONGO, HESSIAN, COLUMBIA, CHLORAZOL, CHLORANTINE, DIANIL, OXAMINE, AND ROSANTHRENE SERIES.	THE PRECEDING COPPERED OR CHROMED.	ALIZARINE PURPLE.	BENZIDINE PUCE.	CHROME BORDEAUX, CHROME PRUNE, ETC.	THIOGENE VIOLET, KATIGENE VIOLET, HYDRONE VIOLET, ETC.	GALLOCYANINE, MODERN VIOLET, ULTRA VIOLET, COREINE, ETC.	CIBA VIOLET, CIBA HELIOTROPE, THIOINDIGO VIOLET, HELINDONE VIOLET.	GALLEIN, ALIZARINE VIOLET, ALIZARINE CLARET, ALIZARINE CYCLAMINE, ALIZARINE RED ON CR MORDANT.	ALIZARINE CYANINE SR, ALIZARINE BORDEAUX.	THIOGENE DARK RED, ETC.	INDANTHRENE VIOLET OR VIOLANTHRENE.

TABLE XVIII.—BLUE COLOURS.

Boil with weak ammonia (1 : 100).																	
The colour is stripped: **Acid Dyestuff** (or Prussian Blue).		The colour is not stripped. Boil for a quarter of a minute with saline caustic soda, rinse with cold water (or salt solution), and boil for one minute with water and one or two drops of weak formic acid (1 : 100).															
The extract is colourless, but becomes blue on acidification. Transferred to wool, the blue is decolourised by Hydrosulphite A, and restored by persulphate: **Triphenylmethane Class.**	The extract is colourless and remains so on acidification. $FeCl_3$ gives a blue precipitate.	The colour is completely or largely stripped, giving a coloured acid extract, which is precipitated by tannin solution: **Basic Dyestuff** (on tannin or other mordant) or **Basic Mordant Dyestuff.** Add chromium fluoride reagent to the extract.					A coloured acid extract precipitable by tannin is not obtained. Reduce original fibre with Hydrosulphite BX.										
		Not precipitated: **Basic Dyestuff.** Transfer to wool and boil with Hydrosulphite AX.			Precipitated. Cr present in ash: **Basic Mordant Dyestuff.** Boil cotton with Hydrosulphite BX.		Decolourised and colour not restored by air or persulphate: **Azo Class.** Boil with soap solution and white mercerised cotton.			Decolourised or yellowish. Colour is restored on exposure to air: **Azine, Oxazine, Thiazine,** or **Indigo Class.** Apply lead acetate test.			Colour changed to greenish yellow, which can be diazotised and developed red with betanaphthol: **Primuline Azo Colour.**	Colour unaffected or becomes darker, browner, etc., the original colour being restored on exposure to air: **Anthracene Mordant** or **Anthracene Vat Dyestuff** (also **Ultramarine**). Boil with 90 per cent. formic acid.			
		Decolourised. Colour returns on exposure to air: **Azine, Oxazine, or Thiazine Class.**	Colour changes to red just before being decolourised. Colour returns violet or blue: **Safranine Azo Dyestuff.**	Decolourised. Colour does not return on exposure to air, but is restored by persulphate: **Triphenylmethane Class.**	Decolourised. Colour returns on exposure to air: **Oxazine Class.**	Decolourised slowly. Colour restored only by persulphate: **Triphenylmethane Class.**	The white cotton is stained: **Salt Dyestuff.** Test ash for Cr and Cu.		The white cotton is not stained. Colour is stripped by boiling pyridine: **Insoluble Azo Colour.**	H_2S is evolved: **Sulphide Dyestuff.**	No H_2S is evolved. Heat fibre carefully in dry test-tube.			The colour is stripped. Al in ash. Apply lead acetate test.		The colour is not much affected. Test ash for Cr.	
							No Cr or Cu present: **Azo Salt Dyestuff.**	Cr or Cu present: **Azo Salt Dyestuff after-treated.**			Violet vapours evolved: **Indigoid Dyestuff.**	No coloured vapour. Cr in ash: **Mordant Thiazine or Oxazine** (not falling in group 6).		H_2S is evolved.	No H_2S evolved: **Alizarine Dyestuff on Al.**	Cr present in ash: **Alizarine Dyestuff on Cr.**	Cr absent: **Anthracene Vat Dyestuff**
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.	17.	18.
ALKALI BLUES, SOLUBLE BLUES, CHLORAZOL BRILLIANT BLUE, ISAMINE BLUE, BETAMINE BLUE, BRILLIANT DIANIL BLUE, BRILLIANT SKY BLUE.	PRUSSIAN BLUE.	METHYLENE BLUE, NEW METHYLENE BLUE, NILE BLUE, CAPRI BLUE, INDAZINE, BASLE BLUE, METAPHENYLENE BLUE, MELDOLA'S BLUE, FAST BLUE, CRESYL BLUE, RHODULINE BLUE, NITROSO BLUE, ETC.	INDOINE BLUE, JANUS BLUE, NAPHTHINDONE BLUE, DIAZINE BLUE, ETC.	VICTORIA BLUE, NIGHT BLUE, TURQUOISE BLUE, SETOCYANINE, ETC.	GALLOCYANINE, GALLAMINE BLUE, CELESTINE BLUE, PRUNE, COREINE, ULTRACYANINE, MODERN CYANINE, ETC.	CHROME BLUE.	BLUES OF THE DIAMINE, BENZO, CONGO, COLUMBIA, CHLORAZOL, DIANIL, OXAMINE, CHICAGO, ETC., SERIES.	THE PRECEDING COPPERED OR CHROMED.	DIANISIDINE BLUE, BLUE FROM NAPHTHOL AC.	BLUES OF THE IMMEDIAL, KATIGENE, THIOGENE, PYROGENE, SULPHUR, ETC. SERIES, HYDRONE BLUES.	INDIGO (NATURAL AND SYNTHETIC), INDIGO MLB 2B, 4B, 5B, 6B, AND T, CIBA BLUE, BROMINDIGO FB.	BRILLIANT ALIZARINE BLUE, GALLOCYANINE, GALLAMINE BLUE, PRUNE, ULTRACYANINE, MODERN CYANINE, CELESTINE BLUE, DELPHINE BLUE, GALLOPHENINE, ETC.	PRIMULINE DEVELOPED WITH NAPHTHYLAMINE ETHER.	ULTRAMARINE.	ALIZARINE CYANINES OR ANTHRACENE BLUES ON AL MORDANT, ERGANONE BLUES.	ALIZARINE BLUE, ALIZARINE CYANINES OR ANTHRACENE BLUES ON CR MORDANT.	INDANTHRENE BLUES, ALGOLE BLUES.

TABLE XIX.—GREEN COLOURS.

Boil with weak ammonia (1 : 100).																			
The colour is stripped: **Acid Dyestuff.** The colour transferred to wool is decolourised by Hydrosulphite A and restored by persulphate: **Triphenylmethane Class.**	The colour is not stripped. Boil for half a minute with saline caustic soda, rinse, and boil twice with weak formic acid.																		
	The colour is completely or largely stripped, giving a coloured acid extract, which is precipitated by tannin solution: **Basic Dyestuff** (on tannin or other mordant) or **Basic Mordant Dyestuff.** Add chromium fluoride to the extract.				A coloured acid extract precipitable by tannin is not obtained. Reduce original fibre with Hydrosulphite BX.														
	Not precipitated: **Basic Dyestuff.** Transfer to wool and boil with Hydrosulphite AX.			Precipitated. Cr in ash. Fibre decolourised by Hydrosulphite BX, the colour not returning in air, but restored by persulphate: **Triphenylmethane Class.**	Decolourised and colour not restored by air or persulphate: **Azo or Nitroso Class.** Boil with soap solution and white mercerised cotton.				The colour is changed to greenish yellow, not restored to green by air, which can be diazotised and developed red with beta-naphthol: **Primuline Azo Class.**	Decolourised. Colour returns on exposure to air: **Azine, Oxazine, or Thiazine Class.** Apply lead acetate test.		The colour is unaffected or changed to red, brown, blue, etc. Test ash for Cr and Ni							Reduced to yellow. Restored by air oxidation: **Indigoid Dyestuff.**
	Decolourised. Colour returns on exposure to air: **Azine, Oxazine, or Thiazine Class.**	Colour becomes red just before being decolourised. Colour returns violet or green on exposure to air: **Safranine Azo Class.**	Decolourised. Colour does not return on exposure to air, but is restored by persulphate: **Triphenylmethane Class.**		The white cotton is stained: **Salt Dyestuff.** Test ash for Cr and Cu.		The white cotton is not stained. Boil with hydrochloric acid (1 : 20).			H_2S is evolved: **Sulphide Dyestuff.**	No H_2S is evolved: **Mordant Oxazine (or Thiazine).**	The ash contains Cr or Ni: **Anthracene Mordant Dyestuff.**				No Cr or Ni present in ash: **Anthracene Vat Dyestuff.**			
					Cr and Cu absent: **Azo Salt Dyestuff.**	Cr or Cu present: **Azo Salt Dyestuff after-treated.**	Colour destroyed. Fe is present in the ash: **Nitroso Class.**	Not decolourised. Cr is present in the ash: **Mordant Azo Dyestuff.**				Reduced colour is brownish red. Green restored by persulphate, but not by air. Boiling HCl (1 : 20) gives bright green solution.	Reduced colour is brown. Green shade returns on exposure to air. Boil with hydrochloric acid (1 : 20).			Reduced colour is brownish olive. H_2S evolved on applying lead acetate test.	Reduced colour is dark maroon. Green shade restored by air.	Reduced colour is blue. Green shade restored by air.	
													Colour unaffected. Solution colourless Cr in ash.	Colour of fibre becomes grey, solution red. Ni in ash.	Colour of fibre rather paler, solution brownish yellow.				
1.	2.		4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.	17.	18.	19.	20.
ACID GREENS, GUINEA GREEN, NEPTUNE GREEN, NAPHTHALENE GREEN, AGALMA GREEN.	FAST GREEN M, METHYLENE GREEN, AZINE GREEN, CAPRI GREEN, ETC.	JANUS GREEN, DIAZINE GREEN, ETC.	BRILLIANT GREEN, MALACHITE GREEN, METHYL GREEN, VICTORIA GREEN, SETOGLAUCINE, NEW FAST GREEN, ETC.	CHROME GREEN.	DIAMINE GREEN, BENZO GREEN, COLUMBIA GREEN, CHLORAMINE GREEN, ETC.	THE PRECEDING COPPERED OR CHROMED.	RUSSIAN GREEN, FAST GREEN O, STEAM GREEN, ALSACE GREEN, GAMBINES, DIOXINE, ETC.	DIAMOND GREEN, ETC.	PRIMULINE DEVELOPED WITH AMIDODIPHENYLAMINE.	GREENS OF THE IMMEDIAL, KATIGENE, THIOGENE, PYROGENE, CROSS-DYE, SULPHUR, AND THIONOL SERIES.	GALLANILIC GREEN, INDALIZARINE, ETC.	ALIZARINE VIRIDINE, BRILLIANT ALIZARINE VIRIDINE, ALIZARINE CYANINE GREEN.	ALIZARINE GREEN S ON CR MORDANT.	ALIZARINE GREEN S ON NI MG MORDANT.	CŒRULEINE, ANTHRACENE GREEN.	INDANTHRENE OLIVE OR OLIVANTHRENE.	INDANTHRENE GREEN OR VIRIDANTHRENE, LEUCOOL DARK GREEN B.	ALGOLE GREEN.	CIBA GREEN, HELINDONE GREEN.

TABLE XX.—BROWN COLOURS.

Boil with weak ammonia (1 : 100).														
The colour is stripped: **Acid Dyestuff.** Transferred to wool it is permanently decolourised by Hydrosulphite AX: **Azo Class.**	The colour is not stripped. Boil for half a minute with saline caustic soda, rinse, and boil twice with weak formic acid (1 : 100).													
	The colour is stripped, giving acid extract which is precipitated by tannin solution: **Basic Dyestuff.** The dyestuff transferred to wool is permanently decolourised by Hydrosulphite AX: **Azo Class.**	A coloured acid extract precipitable by tannin is not obtained. Reduce original fibre with Hydrosulphite BX.												
		Decolourised and colour not restored on exposure to air or by persulphate: **Azo Class and Mineral Colours.** Boil with soap solution and white mercerised cotton.						The shade is changed to greenish yellow, which can be diazotised and developed red with betanaphthol: **Primuline Azo Colour.**	Decolourised and original colour restored by air: **Indigoid Class.**	Unaltered or changed in shade, becoming darker, paler, yellower, etc. Apply lead acetate test.				
		The white cotton is stained: **Salt Dyestuff.** Test ash for Cr and Cu.		The white cotton is not stained. Boil with pyridine.						H_2S is evolved: **Sulphide Dyestuff.**	No H_2S is evolved. Test ash for Cr and Cu.			
		Cr and Cu absent: **Azo Salt Dyestuff.**	Cr or Cu present: **Azo Salt Dyestuff after-treated.**	The colour is stripped: **Insoluble Azo Colour.** Test ash for Cu.		The colour is not stripped: **Mineral Colour.** Treat with sodium bisulphite in the cold.					Cr or Cu (or both) present: **Mordant Dyestuff.** Boil with HCl (1 : 20).			Cr and Cu absent: **Anthracene Vat Dyestuff,** etc.
				Cu absent.	Cu present.	Decolourised.	Not decolourised.				Completely stripped.	Not stripped or only slightly. Boil with dilute caustic soda (10 per cent.).		
												Fibre and solution dull violet.	Solution brown, fibre unaffected.	
1.	2.	3.	4.	5.	6.	7.	8.	9	10.	11.	12.	13.	14.	15.
FAST BROWN, NAPHTHYLAMINE BROWN, ACID BROWN, etc.	**BISMARCK BROWN, JANUS BROWN, TANNIN BROWN,** etc.	**BROWNS** of the **DIAMINE, BENZO, CONGO, DIANIL, CHLORAZOL, COLUMBIA, HESSIAN, OXAMINE,** and **TOLUYLENE SERIES.**	The preceding **COPPERED** or **CHROMED.**	**PARA BROWN** (Chrysoidine and Paranitraniline), **BENZIDINE** or **TOLUDINE BROWN.**	**PARANITRANILINE CUTCH** (Para Red coppered).	**MANGANESE BRONZE.**	**IRON BUFF, KHAKI** (Oxides of Cr and Fe).	**PRIMULINE** developed with Metaphenylene Diamine, **TERRA-COTTA,** etc.	**HELINDONE BROWN G, CIBA BROWN, THIOINDIGO BROWN.**	**IMMEDIAL CUTCH, CROSS-DYE BROWN, KATIGENE BROWNS, PYROGENE BROWNS, THIOGENE BROWNS,** etc.	**ANTHRAGALLOL, ANTHRACENE BROWN, ALIZARINE BROWN.**	**ALIZARINE ORANGE** on Cr Mordant, **ALIZARINE RED** or **PURPURINE** on Cr.	**CUTCH.**	**INDANTHRENE MAROON, ALGOLE BROWN, LEUCOLE BROWNS, CIBANONE BROWN, PARAMINE BROWN** (p-Phenylene Diamine oxidised on Fibre).

TABLE XXI.—BLACK AND GREY COLOURS.

<table>
<tr><td colspan="15">Boil with weak ammonia (1 : 100).</td></tr>
<tr><td rowspan="6">The colour is stripped: Acid Dyestuff. The dyestuff transferred to wool and boiled with Hydrosulphite AX is permanently decolourised: Azo Class.</td><td colspan="14">The colour is not stripped. Boil with dilute hydrochloric acid (1 : 5).</td></tr>
<tr><td colspan="3" rowspan="4">The colour is stripped.</td><td colspan="11">The colour is not stripped (or only slightly). Boil for one minute with saline caustic soda, rinse, and boil with water and dilute hydrochloric acid (1 : 20).</td></tr>
<tr><td colspan="2" rowspan="3">The colour is largely stripped and the acid extract is precipitated by tannin solution: Basic Dyestuff. Transfer to wool and boil with Hydrosulphite AX.</td><td colspan="9">A coloured acid extract precipitable by tannin is not obtained. Reduce original fibre with Hydrosulphite BX.</td></tr>
<tr><td colspan="3">Decolourised and colour not restored by air or persulphate: Azo Class. Boil with soap solution and white mercerised cotton.</td><td rowspan="3">Decolourised and colour restored by air. Gives violet vapours on heating in dry tube: Indigold Dyestuff.</td><td colspan="5">The colour is unaffected or changed in shade (becoming brown, maroon, etc.).</td></tr>
<tr><td colspan="2">The white cotton is stained. Test ash for Cr and Cu.</td><td rowspan="2">The white cotton is not stained. Colour is stripped by boiling pyridine: Insoluble Azo Colour.</td><td colspan="2">The reduced colour is brown, but is rapidly restored to black on exposure to air: Azine, Oxazine, or Thiazine Class. Apply lead acetate test.</td><td rowspan="2">The reduced colour is brown. Only slowly and imperfectly restored to black by air, but at once by persulphate. Cr present in ash; Naphthalene Mordant Dyestuff.</td><td colspan="2">Colour not changed by reduction (or very slightly): Anthracene Class. Test ash for Cr.</td></tr>
<tr><td>Fibre and solution colourless.</td><td>Solution orange. Fe in ash.</td><td>Solution red. Cr in ash.</td><td>Decolourised. Colour returns on exposure to air: Azine, Oxazine, or Thiazine Class.</td><td>Colour becomes red just before being decolourised. Violet or violet blue colour returns in air: Safranine Azo Class.</td><td>Cr and Cu absent: Azo Salt Dyestuff.</td><td>Cr or Cu present: Azo Salt Dyestuff after-treated.</td><td>H_2S is evolved. Fibre becomes colourless or pale buff on boiling with bleaching powder solution 5° Tw: Sulphide Dyestuff.</td><td>No H_2S is evolved. Fibre becomes reddish brown on boiling with bleaching powder solution 5° Tw.: An Oxidation Black.</td><td>Cr present: Anthracene Mordant Dyestuff.</td><td>Cr absent: Anthracene Vat Dyestuff.</td></tr>
<tr><td>1.</td><td>2.</td><td>3.</td><td>4.</td><td>5.</td><td>6.</td><td>7.</td><td>8.</td><td>9.</td><td>10.</td><td>11.</td><td>12.</td><td>13.</td><td>14.</td><td>15.</td></tr>
<tr><td>NAPHTHOL BLACKS, NAPHTHYLAMINE BLACKS, PALATINE BLACK, ETC.</td><td>TANNATE OF IRON.</td><td>LOGWOOD BLACK ON IRON MORDANT.</td><td>LOGWOOD BLACK ON CHROME MORDANT, NOIR REDUIT.</td><td>METHYLENE GREY, NEW METHYLENE GREY, NEW FAST GREY, NIGRISINE, ETC.</td><td>JANUS BLACK, JANUS GREY, DIAZINE GREY.</td><td>BLACKS OF THE DIAMINE, OXYDIAMINE, BENZO, COLUMBIA, DIANIL, PLUTO, ETC., SERIES. ALSO DIAMINOGEN, DIAZO BLACKS, ETC. (DEVELOPED OR COUPLED).</td><td>THE PRECEDING COPPERED OR CHROMED.</td><td>AZO PHOR BLACK, ETC.</td><td>CIBA GREY G AND B.</td><td>BLACKS OF THE IMMEDIAL, KATIGENE, CROSS-DYE, PYROGENE, THIOGENE, THIONOL, PYROL, SULPHUR, ETC., SERIES.</td><td>AGED ANILINE BLACK, PRUSSIATE BLACK, ONE BATH ANILINE BLACK, STEAM ANILINE BLACK, DIPHENYL BLACK.</td><td>NAPHTHAZARINE S, ALIZARINE BLACK S, ALIZARINE BLUE BLACK SW, NAPHTHOMELANE.</td><td>ALIZARINE CYANINE BLACK, ALIZARINE BLUE BLACK B.</td><td>INDANTHRENE GREY, INDANTHRENE BLACK, CIBANONE BLACK, HELINDONE BLACK.</td></tr>
</table>

Notes on the Analytical Tables.

Table XV.

Div. 1.—Brilliant Yellow is largely stripped by weak ammonia, but if white cotton is present it will be stained.

Div. 2.—Sulphide Yellows of the thiazol class, such as Katigene Yellow 2G, Pyrogene Yellow, etc., stain white cotton slightly when boiled in soap.

Div. 3.—Auramine G is almost completely stripped by saline caustic soda, and the formic extract therefore gives no precipitate with tannin solution.

Div. 4.—Diamond Flavine, if not fully fixed, may stain cotton from a soap solution.

Div. 5.—Helindone Yellow and Helindone Orange give yellow vapours on heating the fibre in a dry tube. Upon reduction with Hydrosulphite BX, Helindone Yellow becomes olive, Helindone Orange colourless.

Div. 6.—Indanthrene Yellow (Flavanthrene) is reduced by Hydrosulphite BX to a blue, Indanthrene Golden Orange remains unchanged.

Table XVI.

Div. 1.—Janus Claret Red does not transfer to wool very easily.

Table XVII.

Div. 1.—Alizarine on chromium becomes rather browner on reduction with Hydrosulphite BX.

Table XVIII.

Div, 1.—Alkali Blue dyed on a tannin and tin mordant is only partly stripped by weak ammonia, the solution being colourless.

Table XIX.

Div. 1.—Greens of the nitroso group (Gambines, etc.) may become black on reduction if the Hydrosulphite BX is insufficiently acid (formation of ferrous sulphide).

Table XX.

Div. 1.—Iron Buff and Khaki may become black on reduction if the Hydrosulphite BX is insufficiently acid (formation of ferrous sulphide).

Table XXI.

Div. 1.—Chrome Black (By) becomes light brown on reduction with Hydrosulphite BX, and persulphates change the colour to dark brown but not to black.

Div. 2.—Alizarine Black S [M] returns rapidly after reduction and gives the sulphide reaction with stannous chloride. It therefore appears to fall into Division 10.

CHAPTER VII.

THE ANALYSIS OF INDIGO IN SUBSTANCE AND UPON THE FIBRE.

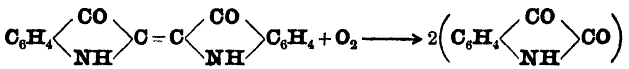
INDIGO, on account of its fastness to light and washing, beauty of shade and other special properties, has long held a predominant position amongst blue dyestuffs. In view of this importance and of its high price much attention has been given to devising means for accurately estimating the amount of the pure colouring-matter present in commercial Indigos or upon dyed materials. In the pages which follow no attempt will be made to enumerate or review the numerous methods which have been proposed by different authors for these purposes, but attention will be confined to a description of those processes which in the author's experience have proved most valuable for practical use.

Valuation of Commercial Indigos.

Synthetic Indigo, which now forms the chief source of supply, comes into commerce in the form of a fine powder containing from 96 per cent. to 98 per cent. of pure Indigo (indigotine). It is also sold as a thin paste containing 20 per cent. of dyestuff, or in the form of a concentrated solution of the leuco compound ("Reduced Indigo"). Natural Indigo is less pure and is generally imported into Europe in the form of lumps or cubes containing, according to its place of origin, from 30 per cent. to 75 per cent. of indigotine. Thus Java Indigo contains on an average from 65 per cent. to 75 per cent., Bengal Indigo from 60 per cent. to 65 per cent., and Madras Indigo from 30 per cent. to 40 per cent. of indigotine. The remaining constituents of natural Indigos are Indigo Red (indirubine), small quantities of certain brown and yellow colouring-matters, glutinous materials and mineral matter (clay and sand). The indirubine in Indian Indigos does not usually exceed 1 or 2 per cent., but in Java Indigo is frequently higher.

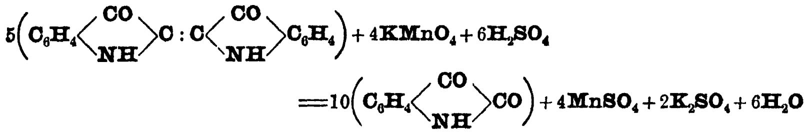
Chemically pure Indigo or indigotine crystallises in purplishblue needles having a coppery reflex. It is insoluble in water, alcohol, dilute acids, and alkalies. In glacial acetic acid, pyridine, phenol, cresol, aniline, and nitrobenzene it dissolves upon heating, but crystallises out again in great part on cooling. Upon strong heating it sublimes, forming a violet vapour which condenses to a crystalline deposit on the cool sides of the tube.

The most convenient methods of estimating indigotine in commercial Indigos are those which depend upon its oxidation to isatine according to the equation:—



$$C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C=C\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C_6H_4+O_2\longrightarrow 2\left(C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle CO\right)$$

For effecting this oxidation a standard solution of potassium permanganate is employed, the reaction with which should proceed theoretically according to the equation:—



$$5\left(C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C:C\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C_6H_4\right)+4KMnO_4+6H_2SO_4$$
$$=10\left(C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle CO\right)+4MnSO_4+2K_2SO_4+6H_2O$$

In order to render the Indigo soluble in water it is first converted into a disulphonic acid (Rawson), or into a tetrasulphonic acid (Bloxam). The product of oxidation is therefore isatin-mono- or di-sulphonic acid. On account of the high dilution, or for other unascertained reasons, the reaction does not take place strictly in accordance with the above equation, and a factor is therefore used which represents the results obtained experimentally with pure indigotine under the same conditions. This factor varies somewhat with the method of analysis employed.

I. Disulphonic Acid Method (Rawson [1]).—0·5 gram of the Indigo in fine powder, dried at 110°, is weighed into a small beaker, and to it are added about 3 grams of white quartz sand and 20 c.c. of pure concentrated sulphuric acid. After mixing with a glass rod, the beaker and its contents are placed in a water oven and heated at a temperature of 70° to 75° C. for an hour, the mixture being meanwhile occasionally stirred. The sulphuric acid solution is then poured off from the sand into a half-litre flask, the sand remaining washed with water and the whole diluted to about 400 c.c.

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[1] C. Rawson, *J. Soc. Dyers and Cols.*, 1885 pp. 74 and 201; *J. Soc. Chem. Ind.*, 1889, p. 251.

10 c.c. of a 10 per cent. solution of barium chloride are then added and the whole made up to 500 c.c. The barium sulphate formed settles quickly and carries down with it impurities present in the Indigo which would otherwise mask the end point of the titration. After standing for half an hour, 50 c.c. of the clear solution are drawn off, diluted with 300 c.c. of distilled water, and titrated with N/50 potassium permanganate (0·632 gram per litre). The end point is obtained when the solution has a pale yellow or orange colour free from any bluish or greenish tint. The quantity of indigotine present is given by the factor: 1 c.c. N/50 $KMnO_4$ = 0·00147 gram indigotine.

With natural Indigos containing more than 1 or 2 per cent. of indirubine the end point instead of being yellow is orange or red, which tint, however, changes to yellow upon further addition of permanganate. It is possible in this manner to estimate approximately the amount of indirubine present. For more exact estimation of the latter the colorimetric method given by Perkin and Bloxam is to be followed.

II. Tetrasulphonic Acid Method (Bloxam[1]).—1 gram of the powdered Indigo, dried at 110°, is weighed out into a small spouted beaker. 2 or 3 grams of white quartz sand are added, and 5 c.c. of fuming sulphuric acid (20 per cent. SO_3 for fairly pure Indigos or 25 per cent. SO_3 for crude Indigos). The mixture is stirred with a short glass rod, then covered with a watch glass and heated in the water oven for three-quarters of an hour at 96° to 98°, stirring at intervals. After cooling, the sulphonic acid solution is transferred to a 500-c.c. flask containing a little water, and to it is also added the washings of the beaker, glass rod, and sand. The whole is then made up to 500 c.c. 100 c.c. of this solution are placed in a conical beaker, together with 100 c.c. of a solution of potassium acetate containing 450 grams per litre. The mixture is heated just to the boiling-point in order to dissolve the precipitate first formed, then cooled at once in running water, and finally allowed to stand for an hour upon ice. If the acetate solution is boiled for any length of time there is a liability for destruction of Indigo to occur. The potassium tetrasulphonate, which separates out upon cooling as a crystalline precipitate, is collected in a Gooch crucible and washed with an ice-cold solution containing 225 grams of potassium acetate

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[1] W. P. Bloxam, *J. Soc. Chem. Ind.*, 1906, p. 735; 1907, p. 1174.

and 12½ grams of glacial acetic acid per litre. If the Indigo is pure, the filtrate is nearly colourless, or at most has only a pale blue tint. With impure Indigos the colour of the filtrate will depend upon the character of the impurities; thus if indirubine is present a red filtrate is obtained. The Gooch crucible containing the tetrasulphonate is now placed in a funnel, resting in the neck of a 200-c.c. flask, and the contents are washed out with hot water, adding any precipitate which may have remained adhering to the conical beaker. The whole is then made up to 200 c.c. 20 c.c. of this solution are transferred to a shallow porcelain dish, acidified with 0·5 c.c. of pure concentrated sulphuric acid, diluted with 80 c.c. of water, and titrated with a potassium permanganate solution containing 1 gram $KMnO_4$ per litre. The quantity of indigotine present is given by the factor: 1 c.c. of 0·1 per cent. $KMnO_4 = 0{\cdot}00222$ gram indigotine. If the titration is effected with N/50 $KMnO_4$, the required factor will be: 1 c.c. N/50 $KMnO_4 =$ 0·00140 gram indigotine.

Although the tetrasulphonic acid method is not as rapid as the disulphonic acid method, it is capable of greater exactitude and is to be preferred when impure Indigos are to be estimated. In such cases the end point is often uncertain and difficult to ascertain with precision unless the impurities are first removed. With Indigos of high purity the two methods agree well. In the case of both methods, however, the presence of starch in the product may lead to erroneous (too low) results. In such case it is necessary to previously boil the sample with dilute hydrochloric acid (4 per cent. HCl) for an hour before proceeding to the analysis.

Testing of Indigo-dyed Woollen Materials.

The prevalent practice of "topping" or "bottoming" Indigo-dyed materials with other colouring-matters, which frequently possess a smaller degree of fastness, has called forth an urgent necessity for methods of ascertaining the quantity of Indigo present on such dyed materials and of investigating their other constituents. The above custom derives a certain justification from the demand of the public for reddish navy blue shades not easily dyed with Indigo alone, or for colours of a fastness to rubbing which is very difficult to secure with pure Indigo. At the same time the practice has led to great abuses, and large quantities of cloth are sold as "guaranteed Indigo dyed" or "guaranteed pure Indigo" in which only a small fraction of the total dyestuffs is actually Indigo, whilst in some cases none at all is present. Whereas formerly only a few dyestuffs were used for "topping" or "bottoming" Indigo blues, an enormous range of colouring-matters are now employed for this purpose, some of them red, some violet, and some blue. The analysis of such mixtures has therefore become a very complicated matter, and the simple tests which were formerly in vogue can no longer be trusted to give any reliable information. Thus the "nitric acid spot" test, still largely relied upon by merchants, which depends upon the production of a bright yellow spot with a green rim when the dyed cloth is touched with a drop of concentrated nitric acid, is given not only by Indigo but also by a number of substitutes, so that its indications are absolutely fallacious. Similarly, the "boiling off" with dilute hydrochloric or sulphuric acids, which was formerly considered to remove from the fabric all dyestuffs other than Indigo, is now no longer to be depended upon, since many of the "acid" and "mordant" dyestuffs used in conjunction with Indigo are unaffected by this treatment, and hence would be regarded as Indigo. At the same time, these older tests may be found of service when used together with the newer methods to be described later.

The methods hitherto proposed for the quantitative estimation of Indigo upon animal fibres by extraction with glacial acetic acid, acetic-sulphuric acid, or hydrosulphite, are mostly unsatisfactory, since they do not afford a reliable means of accurately estimating the quantity of Indigo in the presence of other dyestuffs. They are also tedious and slow to carry out, whilst they are liable to be rendered inaccurate by the contamination of the extracted Indigo with decomposition products of the wool fibre. These difficulties are overcome by the employment of the methods worked out by Green, Gardner, Lloyd, and Frank.[1]

It is clearly of importance not only to be able to estimate the Indigo present upon a textile material, but also to determine the relative proportion of the total shade attributable to Indigo and that due to other dyestuffs accompanying it. Furthermore, it is desirable to ascertain whether the associated

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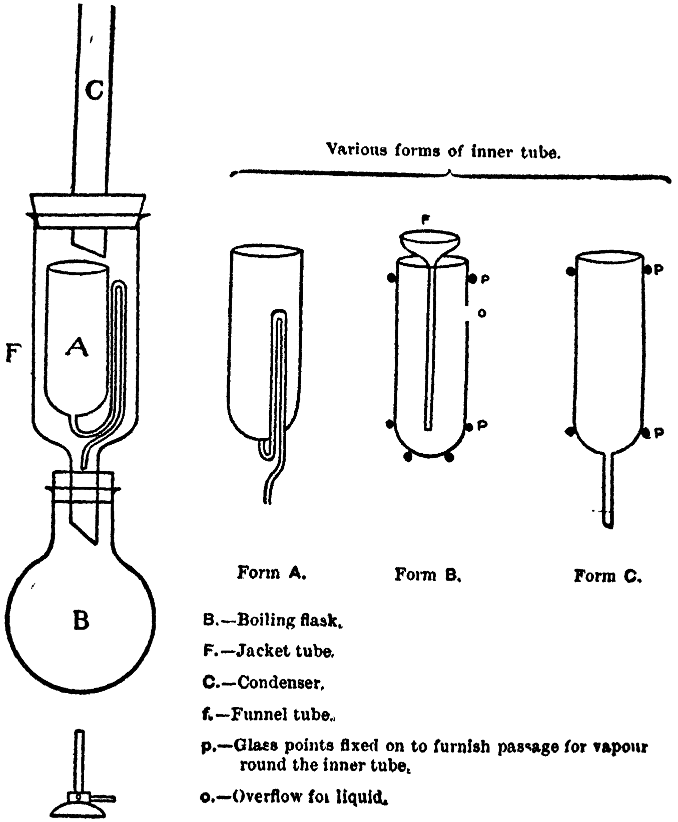
[1] An investigation carried out on behalf of the Textile Institute by A. G. Green, W. M. Gardner, L. L. Lloyd, and G. H. Frank, *J. Soc. Dyers and Cols.*, 1913, p. 226; 1914, p. 15.

dyestuff or dyestuffs are fast to light, washing, and wear. The subject may therefore be considered under three heads, namely: (*a*) estimation of Indigo on the fibre; (*b*) determination of the relative colour effect due to Indigo and to concomitant dyestuff; (*c*) examination of the concomitant dyestuff.



Various forms of inner tube.

Form A. Form B. Form C.

B.—Boiling flask.

F.—Jacket tube.

C.—Condenser.

f.—Funnel tube.

p.—Glass points fixed on to furnish passage for vapour round the inner tube.

o.—Overflow for liquid.

FIG. 1.—Lloyd's Extraction Apparatus.

A. Estimation of Indigo on the Fibre.—The most suitable means of extracting Indigo from the wool fibre for purposes of analysis consists in the employment of pyridine and in effecting the extraction at the boiling-point of the solvent. In the method hitherto employed, the extraction was effected in an ordinary Soxhlet extractor (usually with glacial acetic acid) Under these conditions the operation is unduly prolonged, thus increasing the action upon the wool substance, whilst the extraction is frequently incomplete by reason of the fact that the solvent is much below its boiling-point when it comes in contact with the fibre, which through the long treatment has become shrunk and impervious. This difficulty is overcome by using the modified form of Soxhlet apparatus shown in fig. 1, by means of which the extraction can be effected at the boiling-point of the solvent. The apparatus consists of an outer tube, connected with a Liebig's or air condenser, in which is placed an inner tube containing the cloth or yarn. This inner tube may have the various forms shown (A, B, or C).

The weight of cloth or yarn to be taken for gravimetric estimations varies from 3 to 15 grams, *i.e.* a sufficient quantity to give from 0·03 to 0·10 gram of Indigo. The material is packed loosely into the inner tube: if packed too tightly Indigo may separate in a crystalline form on the interior surface of the tube and is only slowly redissolved. In the apparatus of form A, the hot extract is syphoned intermittently into the distilling flask. With form B, the solvent is directed to the bottom of the tube by means of a long funnel, and then rises through the material, overflowing through the side opening near the top. In the form C, it percolates continuously through the material, flowing out by the small hole at the bottom of the tube. The simpler form of tube C is that which is generally preferred, as it gives good results with all cloths and is easy to make. The tube is drawn out at the end, and some glass points are fused on to the outer surface so as to furnish a passage for the vapour of the solvent. A little white wool, cotton wool, or crushed quartz is placed at the bottom of the tube, as a filtering and regulating medium. The orifice and packing should be so adjusted as to prevent the condensed solvent from running through too quickly and so to allow of the accumulation of a head of liquid above the cloth. The latter is made into a roll which loosely fits the tube. In the extraction of Indigo from heavily felted cloth it is recommended to cut the material into small strips or pieces, and if necessary to stop the extraction after an hour and rearrange the contents of the tube.

Extraction is continued until the extract no longer has a blue colour. The thickest materials can be completely extracted in four hours at most, whilst ordinary materials do not require more than one and a half to two hours.

With the above apparatus satisfactory results can be obtained by the employment of either pyridine or glacial acetic acid as the extracting solvent. Pyridine, however, on account of its higher solvent action and more neutral properties, possesses considerable advantages and is to be generally preferred. It attacks the wool much less, producing less shrinkage, and gives a purer Indigo, requiring less subsequent washing with acids and alkali. It also penetrates the cloth more readily, and hence is capable of entirely removing Indigo from very dense fabrics, when complete extraction by acetic acid is almost impossible. 100 c.c. of commercial pyridine are put into the boiling-flask, which is heated over wire gauze or upon an air bath. When the pyridine runs through colourless, which usually requires about two hours, the extract is distilled down to about 20 or 30 c.c., the pyridine recovered being kept for future use. The extraction flask is then set aside to cool, when the greater part of the Indigo separates in well-formed bronzy crystals. To complete the precipitation 100 c.c. of 50 per cent. alcohol is added, and after heating to boiling, the liquid is filtered either through an ordinary Gooch crucible provided with filter-paper or asbestos, or through a glass filtering-tube containing glass wool. Before weighing the filter for use, it is washed with exactly the same liquids as are to be used for washing the precipitated Indigo, and then dried at 110°. The filtration through a Gooch crucible is very rapid, taking less than two minutes. The precipitate is washed on the filter successively with hot 50 per cent. alcohol, hot 2 per cent. caustic soda, hot dilute hydrochloric acid (1 per cent.), hot water, alcohol, and finally alcohol and ether. The crucible is then dried at 110° and weighed. An alternative method is to wash with cold 20 per cent. sulphuric acid, and then with hot 10 per cent. caustic soda or ammonia, and finally with water and with alcohol. The appearance of the Indigo is a guide to its purity. It should form a bronzy crystalline powder testing 100 per cent. by the tetrasulphonic acid method. A dull appearance shows the presence of impurities.

If it is desired to estimate the Indigo by titration instead of by direct weighing, the precipitate is collected on a Gooch crucible, the bottom of which is covered with a little asbestos. After washing with acids and alkalies as above, and drying for a short time, the crucible is placed in a small beaker containing 15 to 20 c.c. of pure concentrated sulphuric acid, and the Indigo sulphonated by heating in an oven at 70° to 80° C. during three-quarters of an hour. The solution is then made up to half a litre and titrated in the usual way with N/50 permanganate, employing 100 c.c. at a time

TABLE XXII.

(Topped Blues.)

Description.	Percentage of Indigo found.		
	Observer A (by weight).	Observer B (by titration).	Observer B (by weight).
	%	%	%
Cloth dyed with pure Indigo	1·68	1·79	1·73
Same topped with the following dyestuffs:—			
2% Chrome and 2% Sulphoncyanine 5R extra	1·69	1·72	1·72
2% Chrome and 1½% Brilliant Aliz. Blue R pdr.	1·71	1·74	1·67
1½% Topping Violet RTN (B.A.S.F.)	1·67	1·76	1·66
2% Indocyanine 2R (Ber. Co.).	1·68	...	1·72
1½% Erio Fast Purple A (Geigy)	1·69	1·77	1·69
2% Fast Acid Violet R (M.L. and B.)	1·71	1·75	1·72
1¼% Chrome and 2% Chrome Blue A (B.A.S.F.)	1·64	1·73	1·70
1¼% Chrome and 2% Palatine Chrome Blue B	1·59	1·78	1·77
2% Chrome and 2% Hæmatine Crystals	1·70	1·68	1·70
1¼% Chrome and 2% Eriochrome Azurol B	1·65	1·72	1·68
1¼% Chrome and 2% Omega Chrome Cyanine B	1·68	1·67	1·62
2% Chrome and 1¼% Alizarine Blue Black B	1·71	1·68	1·69
2% Chrome and 8% Alizarine Blue GW double	1·67	...	1·65
2% Chrome and 2% Sulphon Dark Blue 2B	1·72	1·69	1·72
2% Chrome and 2% Wool Fast Blue BL (By.)	1·67	1·74	1·62
2% Chrome and 2% Sulphoncyanine GR extra	1·69	1·69	1·65
2% Chrome and 1½% Indochromine 2R conc.	1·73	1·69	1·69
2% Chrome and 20% Cudbear	1·70	1·65	1·65
2% Chrome and 7% Gallein paste	1·67	1·74	1·66
2% Chrome and 7% Gallocyanine paste	1·74	1·73	1·62
2% Chrome and 5% Alizarine Cyanine 3R double paste	1·69	1·73	1·60
2% Chrome and 2% Lanacyl Violet B (Cass.)	1·65	1·76	1·69
2% Chrome and 2% Soluble Blue (L. D. Co.)	1·69	1·73	1·68
2% Chrome and 2% Acid Chrome Blue 2R (By.)	1·65	1·75	1·65
2% Chrome and 2% Eriochrome Blue BR (Gy.)	1·67	1·74	1·62
1% Acid Violet 4BRS (Sandoz)	1·70	1·76	1·72
1½% Omega Light Violet R (Sandoz)	1·72	1·75	1·72
Myrobalans and "Nitrate of Iron"	1·71	1·73	1·66
3% Chrome and 3½% Fustic	1·73	1·72	1·64
2% Picric Acid	1·70	1·76	1·68
2% Chrome and Logwood	1·72	1·70	1·62
Myrobalans and Ferrous Sulphate	1·72	1·65	1·63
Indigo Extract	1·66	...	1·66
Starch	1·62	1·60	1·62
Magnesium Chloride	1·61	...	1·62

diluted with 200 c.c. of water. The percentage of Indigo is found from the factor: 1 c.c. N/50 permanganate corresponds to 0·00147 gram Indigo.

The accuracy of the method is not affected by the presence upon the cloth of other dyestuffs in addition to Indigo. These either remain behind, or if extracted do not separate with the Indigo or are removed therefrom upon washing with acids, alkalies, and alcohol. This is shown by the comparative analyses contained in the two appended tables. In Table XXII. is exhibited a series of analyses by two independent observers of an Indigo-dyed cloth before and after topping with a variety of different colouring-matters. In Table XXIII. is given analyses of cloths dyed with various red dyestuffs which afterwards have all been dyed simultaneously in the same Indigo vat.

TABLE XXIII.

(Bottomed Blues.)

Description.		Percentage of Indigo found.		
		Observer A (by weight).	Observer B (by titration).	Observer B (by weight).
Cloth bottomed with:—		%	%	%
1% Azo Fuchsine G	All dyed together in same Indigo vat.	2·20	2·37	2·14
2% Chrome and 8% Cudbear . . .		2·16	2·02	1·97
2% Chrome and 1% Aliz. Red IWS (M.) .		2·09	2·07	1·94
2% Chrome and 20% Sanderswood . .		2·13	2·00	1·98
2% Chrome and 30% Camwood . . .		2·23	2·05	2·02
2% Chrome and 20% Barwood . . .		2·14	2·05	1·96
1% Chrome and 1% Omega Chrome Red B .		2·20	2·13	2·08

B. Determination of the Relative Colour Effect due to Indigo and to Concomitant Dyestuff.—It is obvious that the simple statement of the percentage of Indigo upon a cloth as found by analysis does not afford to anybody but an expert an idea of the quality of the dye. What is required by manufacturers and merchants, and indeed by the public in general, is a means of ascertaining what proportion of the total depth of colour is due to the Indigo present. The solution of this problem is a difficult one, as besides the difficulty of finding an instrument capable of accurately measuring depth of colour on fabrics, we are also faced with the fact that the dyestuffs accompanying the Indigo are not necessarily blue but are frequently violet or red. In the absence of a more accurate colour-measuring instrument, results of sufficient exactitude for practical purposes are obtainable by the use of the Lovibond tintometer, provided that certain precautions are taken.

FIG. 2.

This instrument consists of a double tube, through one eye-piece of which the pattern is viewed, through the other a piece of white material. Between the latter and the eye can be interposed a series of standard coloured glasses, red, yellow, and blue, by means of which the pattern is matched. A form of this instrument (fig. 2) which is especially suitable for the purpose in view is provided with three apertures instead of two, the central one being used to view the pattern, whilst the two outside ones are employed for the matching glasses. In this way the pattern may be compared with two sets of matching glasses at the same time. The standard glasses bear numbers expressing their depth of shade, and by adding these together the units of red, yellow, and blue required to match the pattern are obtained. Since the relative proportions of red, yellow, and blue light reflected by an indigo blue pattern changes as the shade becomes darker, the red increasing at a greater rate than the blue, it is obvious that as a measure of the depth of shade, only the sum of the total colour units can be employed, which is given by adding together the units of red, yellow, and blue obtained from the glasses required to match the pattern.

A graded series of patterns, dyed with pure Indigo upon white wool, in which the percentage of Indigo present had been carefully determined, gave the following results when measured by the tintometer in a good north light:—

TABLE XXIV.

Number.	Percentage Indigo present (by analysis). (Mean Result.)	Tintometer Measurements.			
		Red.	Yellow.	Blue.	Total Units.
1	0·45	4·0	2·6	10·9	17·5
2	0·55	4·9	2 9	11·4	19·2
3	0·70	6·1	3·4	12·1	21·6
4	0·85	7·1	3 5	12·7	23·3
5	1·05	8·4	3·5	12·96	24·86
6	1·25	9·0	4·0	13·0	26·0
7	1·40	9·6	4·3	13·1	27·0
8	1·70	10·8	4·7	13·5	29·2
9	2·20	11·7	5·9	13·6	31·2
10	2·50	12·2	6·6	13·7	32·5
11	2·71	12·5	8·3	13·0	33·8
12	3·55	13·2	9·4	14·0	36·6
13	4·45	13·7	9·8	14·5	38·0

By plotting the total tintometer units as abscissæ and the Indigo percentages as ordinates a regular curve is obtained (fig. 3). There is thus a definite relation between the percentage of Indigo on the material and the tintometric readings.

Having constructed such a curve from a series of Indigo dyeings of known strength, it can be employed to determine from the tintometer readings given by a certain cloth the percentage ,of

Indigo upon it when the cloth has been dyed with Indigo alone; or when dyed with other colouring-matters in addition, the percentage of Indigo which would be required to give a shade of corresponding depth were Indigo only used. Furthermore, when the actual percentage of pure Indigo upon the cloth has been determined by analysis one can express the colour effect due to the latter (obtained from the curve) as a percentage of the total colour, measured in terms of the amount of Indigo which would be required to give the shade if Indigo alone were employed.

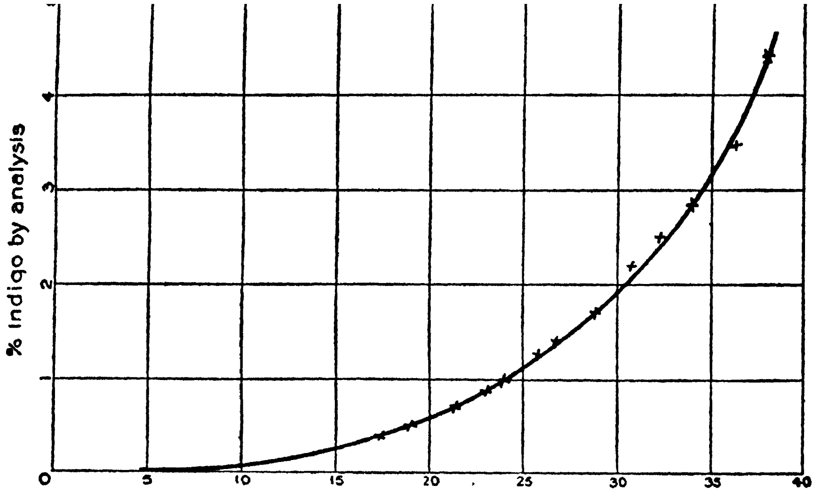


FIG. 3.—Readings on Lovibond's Tintometer (Total Colour Units).

This ratio, termed "the percentage colour effect due to Indigo," is given by the expression: $x = \frac{100A}{C}$, in which A = the percentage of Indigo found by analysis and C = percentage of Indigo given by the curve corresponding to the total tintometer units read. It is obvious that this value could not be obtained from the direct ratio of the tintometer colour units corresponding to the Indigo present and to the total shade, since the depth is not directly proportional to the amount of dyestuffs present, but increases at a constantly diminishing rate as the shade becomes darker. It has been ascertained by examination of a large number of patterns dyed with pure Indigo that the same percentage of Indigo gives substantially the same tintometric reading for all classes of materials composed of wool independently of the quality and weave, or whether dyed in the raw wool, yarn, or piece. It has also been established that in mixed shades the tintometric reading is the same whether the additional dyestuff has been employed as a "bottoming" or as a "topping" colour.

Since the readings obtained with the tintometer vary considerably with the locality, time of year, method of observation, and individual differences of eyesight, it is not possible to give absolute numbers for the correspondence of the Indigo percentage with the depth of shade, or to lay down a fixed curve. Even readings by the same observer on different days may differ considerably through variations in the daylight. It is, therefore, necessary that the curve given above should only be used as an approximation to be corrected at the time of use by taking tintometer readings of a series of four or five standard shades of pure Indigo kept for the purpose, in which the percentages of Indigo have been accurately determined by analysis. Having also obtained by analysis the percentage of Indigo in the material under examination, the value for the "percentage colour effect due to Indigo" can then be deduced from the corrected curve. For example, a sample of cloth dyed with Indigo and topped with other dyestuffs is found to contain 1·5 per cent. of Indigo by analysis, and gives a total reading of 32½ colour units on Lovibond's tintometer. From the curve it is seen that a shade dyed with pure Indigo to give a reading of 32½ colour units has to contain 2·4 per cent. of Indigo. Therefore, "the percentage colour effect due to Indigo" on the pattern is $\frac{1{\cdot}5 \times 100}{2{\cdot}4} = 62{\cdot}5$. All the analyses and tintometer measurements are made upon cloth containing its "condition moisture," usually about 14 per cent. H_2O.

Whilst with blue shades of moderate depth the results obtained by the above procedure are sufficiently accurate, the method ceases to be applicable when the Indigo present exceeds 2 or 2·5 per cent., since with dark shades the curve approaches more and more to the perpendicular, and a relatively large increase in the percentage of Indigo produces only a small increase in the tintometric reading. In such cases another method can be employed, which in fact is capable of general application both for light and heavy shades. This consists in removing the Indigo from the pattern without disturbing the accompanying dyestuff or dyestuffs, the colour effect of which is then determined separately by the tintometer. By means of the curve, the tintometric reading of the residual colour may be expressed as the equivalent in depth of so much Indigo, and the ratio of this to the actual Indigo present obtained. Thus, if B equals the Indigo equivalent of the residual colour left after removal of Indigo, and A equals the Indigo actually present as determined by analysis, then the "percentage colour effect due to Indigo" equals $\frac{100A}{A+B}$.

In order to carry out this second method it is necessary to be able to strip the Indigo completely from a compound shade and to leave the "topping" or "bottoming" colour almost unaltered. A small *change* of shade of the latter does not matter, provided the *depth* is not affected. In a large number of cases this may be satisfactorily accomplished by employing either boiling glacial acetic acid or boiling pyridine as the stripping agent. for whereas many dyes are removed from wool by one or the other of these solvents, comparatively few of them are stripped by both, those which are dissolved by the one being usually not affected by the other. In using these solvents care should be taken that they are anhydrous, as a small percentage of water increases their solvent action on dyestuffs other than Indigo. The acetic acid should therefore be frozen and the separated crystals remelted, whilst the pyridine should be carefully dried over solid caustic soda. For the same reason, the pattern to be extracted should be previously dried in a steam oven.

The extraction is carried out in the same manner as described above for the Indigo estimation. As there are a few colouring-matters which are removed from the wool by both glacial acetic acid and by pyridine, some other solvent of more general applicability is also desirable. This is afforded by cresol mixed with a certain proportion of a hydrocarbon of lower boiling-point. One hundred parts cresol (best commercial cresylic acid, 97 to 98 per cent.) with 30 parts of "solvent naphtha" of boiling-point 125° to 140° C., or 75 parts of cresol with 25 parts of "turpentine substitute" or heavy petroleum spirit of boiling-point 155° to 170° C., have proved to be suitable mixtures. The extraction is effected in this case with an *ordinary* Soxhlet extractor, which is provided with an air or water condenser. The sample, previously dried in a steam oven, is laid on a little loose wool and covered lightly with a further layer of loose wool, a thermometer being placed with its bulb in contact with the pattern. The proportion of hydrocarbon to cresol is so adjusted that the temperature of the extracting liquid round the pattern does not exceed 110° C., and is preferably about 100° to 105° C. The lower the temperature at which the extraction of the Indigo can be effected, the less the danger of disturbing the concomitant dyestuffs. Care should be taken not to continue the extraction after the Indigo has been completely removed, or a loss of residual colour may occur. Carried out with care this method of separation is capable of almost universal application.

The behaviour of the three solvents, acetic acid, pyridine, and cresol mixture, towards a variety of colouring-matters dyed upon wool in conjunction with Indigo is shown in Table XXV. The minus sign indicates that the colour is stripped, the plus sign that it is not affected or only slightly, and the sign (+ −) that it is partially removed. Those dyestuffs marked by an asterisk are changed in shade. In all cases the Indigo was completely removed by the solvent.

Only the "acid" and "mordant" dyestuffs are here taken into consideration, as "basic" dyestuffs are very rarely employed. In the exceptional case of a "basic" dyestuff being used as a "topping" or "bottoming" colour for Indigo, it will be removed from the fibre completely by all three solvents, and it would therefore be necessary to employ a somewhat different method of examination, as, for instance, to extract the "basic" dyestuff first by means of alcohol or 1 per cent. hydrochloric acid, after which it could be transferred from the solution to white wool in order to estimate its amount.

The association with or substitution for Indigo of other "vat" dyestuffs need also not be considered, as owing to their high price they scarcely come into consideration in this connection. Only the mono- and dibromo-indigos are occasionally used to give redder shades. These would be extracted by pyridine and included with the Indigo if weighed directly, but in view of their close similarity to Indigo, and even greater fastness, there would be little objection to their being returned as such. Tetrabromo-indigo (Ciba Blue, Brom Indigo FB) can be separated from Indigo by heating with concentrated sulphuric acid, which sulphonates the latter only, the percentage of which can then be found by titration with permanganate.

TABLE XXV.

Name of Colouring-matter.	Acetic Acid.	Pyridine.	Cresol Mixture.
Sulphonçyanine 5R extra (By.)	−	−	+
Brilliant Alizarine Blue R (By.)	+ −	+ −	+
Topping Violet RTN (B.A.S.F.)	+	−	+
Indocyanine 2R (Ber.)	+	+	+
Erio Fast Purple A (Gy.)	+	−	+
Fast Acid Violet R (M.L. and B.)	+ −	+ −	+
Chrome Blue A (B.A.S.F.)	+	+	+
Palatine Chrome Blue 2B (B.A.S.F.)	+	+	+
Hæmatine Crystals	−	+	+
Eriochrome Azurol B (Gy.)	−	+	+
Omega Chrome Cyanine B (Sz.)	+	+	+
Alizarine Blue Black B (By.)	*	+	+
Alizarine Blue SW (B.A.S.F.)	+ −	+	+
Sulphon Dark Blue 2B	−	−	+
Wool Fast Blue BL (By.)	+ *	−	+
Sulphoncyanine GR (By.)	−	−	+
Indochromine 2R conc. (Sz.)	+ *	+	+
Cudbear on Chrome	−	−	+
Azofuchsine	−	−	+
Alizarine Red IWS (M.L. and B.)	+ −	+	+
Sanderswood and Chrome	−	+ −	+ −
Camwood and Chrome	−	+ −	+ −
Barwood and Chrome	−	+ −	+ −
Omega Chrome Red B	+	−	+
Gallein Paste	−	+	+
Gallocyanine	−	+	+
Alizarine Cyanine 3R	−	+	+
Lanacyl Violet B (Cass.)	+	−	+
Soluble Blue	−	−	+ −
Acid Chrome Blue 2R (By.)	+ *	+ −	+
Eriochrome Blue BR (Gy.)	+	−	+
Acid Violet 4BRS (Sz.)	+	−	+
Omega Light Violet R (Sz.)	+	−	+
Myrabolans and Iron	−	+	+
Fustic and Chrome	−	+	+
Picric Acid	−	−	+ −
Logwood and Chrome	−	+	+
Indigo Extract	+	−	+
Eriochrome Red BR (Gy.)	+	−	+

In order to illustrate the degree of correspondence of the above two methods of estimating the relative depths of shade due to Indigo and accompanying dyestuff, the following analyses made with five navy blue serges are given. These were tested by the tintometer together with the bottom shades (Alizarine Reds) upon which they were dyed, and also the same serge dyed in the white state from the same vat at the same time, and therefore containing approximately the same quantity of Indigo. In each case the total number of tintometer units found were translated by means of the curve into percentage Indigo equivalents, the following numbers being obtained:—

TABLE XXVI.

Number of Sample.	Indigo Equivalents from Curve (percentages).		
	Blue dyed on White Serge.	Red Bottom (=B).	Compound Shade (=C).
1	2·41	0·38	2·84
2	1·55	0·48	2·10
3	1·35	0·50	1·85
4	1·46	0·78	2·30
5	1·96	1·25	3·25

The actual Indigo present on the patterns was found by analysis to be as follows:—

TABLE XXVII.

Number of Sample.	Percentage Indigo present.		
	Blue on White Serge.	Compound Shade.	Average (=A).
1	2·39	2·29	2·34
2	1·52	1·52	1·52
3	1·28	1·33	1·31
4	1·44	1·41	1·42
5	1·85	1·88	1·86

Calculating for these five patterns the "percentage colour effect due to Indigo," firstly from the tintometer readings alone, and secondly by making use of the two equations:—

$$\text{I.}\quad x=\frac{100A}{C} \qquad\qquad \text{II.}\quad x=\frac{100A}{A+B}$$

the following results are obtained:—

TABLE XXVIII.

Number of Sample.	Percentage Colour Effect due to Indigo.		
	From Tintometer Values alone.	By Method I.	By Method II.
1	82·2	84·8	86·0
2	72·4	73·8	76·0
3	70·8	72·9	72·4
4	61·7	63·5	64 5
5	57·2	60·3	59·8

The results by the different methods are therefore in good accord.

The limits of accuracy of the second method is also exhibited by the following series of analyses of various commercial samples (Government and Official cloths) carried out by two independent observers, the first of whom used cresol mixture and the second dried pyridine for removing the Indigo.

TABLE XXIX.

Number of Sample.	Indigo found by Analysis (= A).		Indigo Equivalent of Residual Colour (= B).		Percentage Colour Effect due to Indigo $\left(=\frac{100A}{A+B}\right)$	
	Observer A.	Observer B.	Observer A.	Observer B.	Observer A.	Observer B.
1	2·35	2·52	0 55	0·72	80	77
2	2·54	2·59	0·20	0·22	92	92
3	4·18	4·18	0·68	0·72	86	85
4	3·23	3·35	0·68	0·55	83	86
5	3·23	3·12	0·30	0·36	91	90
6	3·0	3·25	0·65	0·65	82	83
7	4·23	4·20	0·30	0·32	93	93
8	2·54	2·60	0·75	0·48	77	84
9	2·82	2·90	0·60	0·62	81	82
10	2·91	3·03	0·40	0·32	88	90

In using the tintometer the reading should be made in a good north light coming from the front, and the instrument should be placed upright or at an angle not less than 70° to the horizontal, taking care that there is no top light to cast a shadow on the pattern. When a Dufton-Gardner "Dalite" arc lamp is available, this may be used with advantage in place of daylight as a constant source of illumination, the lamp being placed within a foot or so of the tintometer and nearly on a level with it. For further details respecting the use of the tintometer the reader is referred to the *Measurement of Light and Colour Sensations*, by J. W. Lovibond (George Gill & Sons, London).

C. Examination of the Concomitant Dyestuff.—In judging the quality of a navy blue material dyed with Indigo in conjunction with other dyestuffs, it is necessary to consider not only the proportion of Indigo present, but also the degree of fastness of the accompanying dyestuff. It is obvious, for example, that a cloth in which 50 per cent. of the shade is due to Indigo and 50 per cent. to Alizarine Red is to be preferred to another in which 60 per cent. is due to Indigo and 40 per cent. to Logwood. It is therefore necessary for a complete examination of an Indigo-dyed cloth that the identity, or at least the class of the associated dyestuff should be ascertained and tests made for the fastness of the latter to light, washing, etc. Although until recently this was usually an impossible task, the methods described above of separating Indigo from associated dyestuffs render it comparatively easy. The colour left upon the wool after extraction with acetic acid, pyridine, or cresol can be submitted to direct examination in the manner described in Chapter V., and the fastness ascertained by subjecting it to the usual tests for light, soap, washing, etc. In cases in which more than one "topping" or "bottoming" colour has been employed, indications of the composition of the mixture may often be obtained by comparing the residual colour left after extraction by different solvents (acetic acid, pyridine, or cresol).

In many cases when time will not admit of a full analysis, it is desirable to test approximately the quality of the dyed material, and the methods described above may be used by the practical dyer or merchant to obtain quickly a general idea of the composition and fastness of the shade. Small patterns of the material can be stripped in about twenty minutes with the cresol mixture by employing a simple extraction apparatus, or by heating with the solvent in small beakers placed in a water or steam oven. By means of the eye alone a rough estimate can be formed of the relative proportion of Indigo to residual colour, and the latter can also be tested for fastness, and if need be, identified. For work of an approximate character it is also possible to replace the use of the tintometer by a series of standard shades of pure Indigo of known Indigo percentages, with which the pattern may be compared by the unaided eye before and after stripping with cresol. In a few cases, *e.g.* mixtures of Indigo with Logwood or of Indigo with Alizarine Reds, the Indigo may either be removed first by extraction with cresol, leaving the accompanying dyestuff on the fibre, or the latter may be stripped by boiling with dilute sulphuric acid and the Indigo left upon the fibre. It is thus possible when Indigo is accompanied by one of these dyestuffs, together with an "acid" or "acid-mordant" dyestuff, to effect a separation of all three constituents by applying both methods. For example, a blue composed of Indigo, Alizarine Red SW, and Eriochrome Azurol, when boiled with dilute sulphuric acid leaves the Indigo and Eriochrome Azurol upon the fibre whilst the Alizarine Red dissolves. On then extracting the residual colour with cresol the Indigo dissolves, leaving the Eriochrome Azurol.

Estimation of Indigo upon Cotton and Linen.

The pyridine extraction method described above for wool may be employed with equal advantage for the estimation of Indigo upon cotton, the procedure being in every respect the same.

Another method which also gives good results and is equally easy to carry out is that devised by Knecht.[1] This is performed in the following manner:—4 grams of the sample of dyed cloth are cut up into small pieces and placed in a porcelain beaker; 25 c.c. of sulphuric acid of 80 per cent. (61° Bé.) are now added, and the whole stirred slowly, the temperature being maintained at about 40°. After ten to fifteen minutes' stirring all the cloth has gone into solution. The contents of the beaker are now diluted to about 100 c.c. with water, boiled for a few minutes until the precipitated Indigo becomes granular, and filtered through a Gooch crucible containing asbestos or quartz sand covered with a layer of silica as the filtering medium. After drying the precipitate at 110° to 120°, it is sulphonated by heating with concentrated sulphuric acid for an hour in the water oven, and then titrated with permanganate (see p. 77). In order to remove any accompanying dyestuff, it is better to wash the precipitated Indigo prior to drying, with hot

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[1] Knecht, *J. Soc. Dyers and Cols.*, 1909, pp. 135, 160.

dilute ammonia and finally with alcohol. The "topping" or "bottoming" of Indigo blues with other colouring-matters is not as prevalent a practice in cotton as it is in wool dyeing. Nevertheless "sulphide" colours are frequently employed as a bottom, and the possibility of "basic" or "salt" dyestuffs being present must not be overlooked. "Vat" colours, excepting perhaps Thioindigo Red and Bromindigos, by reason of their high cost, need scarcely be considered as possible accompaniments. Neither of the above-mentioned methods of estimating Indigo on cotton are influenced by the presence of "basic," "salt," or "sulphide" dyestuffs. "Vat" colours of the indigoid class are extracted by pyridine and would be estimated as Indigo if weighed directly. If, however, the precipitate obtained either by pyridine extraction or by treatment of the fibre with 80 per cent. sulphuric acid is sulphonated and titrated with permanganate, only the Indigo becomes soluble, whilst Thioindigo Red and Bromindigos remain undissolved and are not estimated.

For ascertaining the depth of colour due to the accompanying dyestuff when this belongs to the "sulphide" or "salt" classes, the fibre is extracted with pyridine until all the Indigo is removed, after which the residual colour is examined and its depth measured in a similar manner to that already described for wool. If a "basic" dyestuff is present, this is best removed first by boiling the fibre with aqueous caustic soda followed by dilute acetic acid or formic acid. The depth of the residual Indigo can then be compared with the depth of the original shade. If it is desired to estimate the amount of "basic" dyestuff more exactly, the pattern must be boiled in "saline caustic soda," and the "basic" dyestuff afterwards transferred to a weighed amount of wool as described in Chapter V.

CHAPTER VIII.

THE ANALYSIS OF PIGMENTS AND LAKES.

ALTHOUGH the analysis of pigments and colour lakes is a matter of growing importance to the manufacturer and user of these products, such analysis has hitherto been attended with considerable difficulties, and could only be attempted with any degree of success by the expert possessing an extensive knowledge of the dyestuffs generally employed in lake-making and of their properties. These difficulties have increased in recent years through the great multiplication of the number of dyestuffs in commerce, and by the introduction of a variety of special products for the lake industry. A laudable attempt to overcome these difficulties has indeed been made by George Zerr,[1] who has published the individual reactions of a large number of the dyestuff lakes now in use. Although, however, the tests proposed may be employed to supplement a systematic group separation, they are of too empirical a nature to serve as a means of classification or separation, and would certainly require long experience before they could be used for the identification of the mixtures so frequently encountered in practice. The scheme which is here presented, and which it is hoped may facilitate such investigations by placing the analysis upon a more systematic basis, depends upon the same principles as those described in earlier chapters for the examination of dyestuffs in substance or upon the fibre; the final reactions for classification and identification being effected after transferring the colour to wool or cotton.

The pigments and lake colours employed for paints, printing inks, lithographic colours, wall-paper stains, etc., consist of (*a*) mineral pigments, (*b*) mineral bases or substrata coloured by organic dyestuffs.

The most important mineral pigments are Chrome Yellow and

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[1] Zerr, *Tests for Coal-Tar Colours in Aniline Lakes.* English translation by Dr Charles Mayer, 1910.

Chrome Orange (lead chromates), Zinc Yellow (zinc chromate), Naples Yellow (lead antimonite), Cadmium Yellow (cadmium sulphide), Prussian or Milori Blue (ferrous ferricyanide), Ultramarine, Bremen Blue (cupric hydroxide), Cobalt Blue (cobalt aluminate), Schweinfurt Green (cupric acetoarsenite), Guignet Green (chromium hydroxide), Chrome Green (Chrome Yellow mixed with Prussian Blue), Zinc Green (zinc chromate and Prussian Blue), Red lead (lead oxide), Vermillion (mercury sulphide), Chrome Red (basic lead chromate), Venetian Red (ferric oxide), Yellow Ochre (clay containing ferric hydroxide), Red Ochre (clay containing ferric hydroxide and ferric oxide), Sienna (mainly ferric hydroxide), Burnt Sienna (mainly ferric oxide), Lamp Black and Ivory Black (carbon), Green Earth or Augite (complex silicate of magnesium, iron, and aluminium or calcium). The examination of these products we need not discuss; they can be identified by the ordinary methods of inorganic analysis.

The pigments and lakes prepared from organic dyestuffs are of a very varied character. The following are the most important classes of dyestuffs used for this purpose:—

(1) *Nitroamines*, such as Pigment Chlorine 2G and Lithol Fast Yellow 2G. These are formaldehyde condensation products of primary nitroamines, such as of nitro-orthotoluidine. They are soluble in boiling benzene (not very readily) and have a yellow colour. They are rather volatile.

(2) *Insoluble Azo Dyestuffs*, such as Hansa Yellow, Pigment Chrome Yellow, Autol Oranges and Reds, Lithol Fast Scarlets, Pigment Reds, Pigment Bordeaux, etc. They are monoazo compounds devoid of salt-forming groups (no SO_3H, $COOH$, or NH_2 groups). They all dissolve readily in hot benzene. The orange and red colours are derived from the diazo compounds of aniline, nitranilines, chloranilines, toluidines, nitrotoluidines, naphthylamines, etc., in combination with β-naphthol. The yellows are obtained from similar diazo compounds combined with phenylmethylpyrazolone. The full analysis of such products can be effected by subjecting them to reduction and isolating their decomposition products according to the methods given in Chapter IX. The dyestuffs of this and of the preceding class are employed in the manufacture of lakes by simply grinding them with a mineral substratum or by mixing them with a substratum in paste form.

(3) *Acid Dyestuffs.*—This is a very large group of compounds mostly belonging to the azo class, but also containing many members of the triphenylmethane, pyrone, anthracene, and other classes. They are entirely insoluble in benzene. From the standpoint of lake manufacture they may be subdivided into the two following categories:—

(*a*) Dyestuffs (mostly azo derivatives of β-naphthol and of β-oxynaphthoic acid) containing only one acid group and consequently sparingly soluble in water. They are represented by a range of red to violet products specially prepared for use as pigments, such as Lithol Reds, Lithol Bordeaux, Permanent Reds 4B and 6B, Lake Reds C, D, and P, Helio Oranges, Reds and Purpurines, etc. These colouring-matters give very sparingly soluble barium, strontium, and calcium lakes, which frequently possess a much bluer shade than the sodium salts. They are either ground directly with the substratum or are precipitated upon it by the addition of a salt of barium, strontium, or calcium. Owing to their sparing solubility they are frequently sold in the form of pastes; the product in some cases being the ready prepared barium or other alkaline-earth salt.

(*b*) Dyestuffs easily soluble in water, usually containing several sulphonic groups. These consist for the most part of the ordinary "acid" dyestuffs employed in dyeing, such as Acid Yellows, Azo Oranges, Azo Scarlets, Azo Reds, Azo Bordeaux, Acid Violets, Acid Greens, Patent Blues, Eosines, Acid Eosines, Acid Rhodamines, Acid Alizarines, etc. They are usually precipitated upon the substratum by means of barium chloride, or of barium chloride in conjunction with alumina or tannin. They may be readily distinguished from the members of the previous category by the greater ease with which they leave the substratum and pass into solution when the lake is heated with weak alkalies such as a 2 per cent. solution of sodium carbonate.

(4) *Basic Dyestuffs*, such as those of the triphenylmethane, azine, oxazine, and thiazine classes. They are usually precipitated upon the substratum by means of tannin and antimony, or by a salt of phosphoric, arsenious, stannic, silicic, resinic, or fatty acid, in presence of aluminium hydroxide. They are also frequently employed for shading acid colours, previously precipitated by barium chloride, in which case no further precipitating agent is needed.

(5) *Mordant Dyestuffs,* chiefly represented in lake pigments by the aluminium compounds of alizarine, purpurines (Alizarine Reds and Madder Reds), Alizarine Orange, Alizarine Bordeaux, Alizarine Cyclamine, Anthracene Blues, Alizarine Cyanines, and Cochineal Carmine. The aluminium lakes of these dyestuffs, though not decomposed by weak alkalies, such as boiling 2 per cent. sodium carbonate, are split up by dilute hydrochloric acid (1 part of commercial acid to 10 parts of water). Under this treatment Alizarine Red or Madder Red becomes yellow, and a small piece of wool added to the solution acquires a yellow colour which is changed to purple by ammonia or caustic soda. Alizarine Bordeaux behaves similarly, but is less easily decomposed. Cochineal Carmine gives to wool an orange tint which also becomes purple with caustic alkalies.

(6) *Vat Dyestuffs.*—The colouring-matters of this class, by reason of their extreme degree of fastness to light and other agencies, have recently attracted much attention for pigment manufacture, especially for the preparation of artist's colours. Their employment, however, is considerably restricted by their high price. Being entirely insoluble in water, they are incorporated with substrata, *e.g.* aluminium hydroxide, by simply mixing them with the latter in a very finely divided form. The "vat" dyestuffs of the indigoid and anthracene classes being mostly devoid of salt-forming groups can be regarded as "neutral" compounds, and hence they are more or less soluble in hydrocarbons. The solubility in benzene of the individual members of this class varies considerably, however, and in the scheme of analysis employed, colours of this group may either fall into the second section or into sections 17 and 18. In either case, however, the dyeing test on cotton affords an easy means of identification. The "vat" dyestuffs belonging to the sulphur class are for the most part insoluble in hydrocarbons such as benzene.

The substrata, upon which the above dyestuffs are distributed or precipitated, may be either (*a*) colourless substances, or (*b*) coloured materials. The most important of the former are barium sulphate ("heavy spar"), calcium sulphate ("satin white"), china clay, kieselguhr, calcium carbonate, lead sulphate, lead carbonate, zinc white, lithopone, calcium phosphate, starch, etc. These are used either ready formed in a finely ground state or are precipitated with the lake by interaction of appropriate salts. The chief coloured substrata are red lead, litharge, ochre, umber, green earth, and lamp black. In addition to these, any other mineral pigments may be employed as a basis upon which to precipitate a dyestuff with the object of adding to the brilliancy of the pigment or of increasing its depth of shade. The search for the dyestuff should always be accompanied or preceded by an examination of the substratum.

In proceeding to the investigation of the dyestuff it must be borne in mind that it is a very common practice to employ more than one colouring-matter, which may belong to the same or to different classes. It is therefore necessary before these dyestuffs can be identified to effect a separation of them so far as may be possible. Whilst the annexed scheme may be employed as a means of separation into classes, the separation of members of the same class is often a more difficult task. For the latter purpose use can sometimes be made of variations in solubility during treatment with the group reagents, or with hot water, alcohol, ether, etc. Thus whilst many "acid" dyestuffs are dissolved from the lake by 2 per cent. sodium carbonate either in the cold or on gently warming, others require to be boiled, or may even necessitate the use of aqueous-alcoholic sodium carbonate to effect solution. In the case therefore of a mixture of an easily soluble and a sparingly soluble "acid" dyestuff, it is possible by proceeding cautiously to effect the extraction of each separately, then to dye each upon wool, and test them individually. Again, different "basic" dyestuffs vary considerably in the ease with which their tannin lakes are decomposed by caustic soda, and when decomposed some yield dye-bases which are soluble in water, whilst the dye-bases of others are insoluble. Upon such differences a separation can often be based, each colour being separately transferred to wool for testing. In other cases again the capillary method of analysis of Goppelsroeder may be found serviceable, the aqueous solution being spotted upon thick filter-paper or strips of filter-paper hung with their lower ends dipping into the solution. Zones of the respective colouring-matters are thus produced, and these zones can then be separately extracted with water and the colours transferred to wool for testing. By making use of such methods of fractional extraction, or of capillary separation, followed by transference to wool, the identification of the constituents of a mixed lake can be effected in a large number of cases. As it frequently happens that dyestuffs of two different shades are present, *e.g.* a blue and a yellow dyestuff in a green pigment, it has been thought best to give a single table of separation, irrespective of shade, although it will be at once apparent that the shade of the pigment affords valuable assistance in identifying certain constituents and in excluding others.

The scheme comprised in the annexed table is primarily intended for the identification of lake pigments derived from organic dyestuffs. Inorganic pigments should be detected during the progress of the inorganic analysis which in all cases is an advisable preliminary in order to establish the nature of the substratum employed. In view, however, of the fact that organic dyestuffs may be used to shade or intensify a mineral pigment, it has been considered advisable to indicate the behaviour of some of the most important mineral pigments towards the reagents employed in the scheme.

Prussian or Milori Blue.—Completely decolourised by boiling with 2 per cent. sodium carbonate. The solution (if filtered from ferric hydroxide) does not regenerate the colour upon acidification, nor dye wool.

Ultramarine Blue and Ultramarine Violet.—Not changed by boiling with 2 per cent. sodium carbonate. Completely decomposed and decolourised upon boiling with dilute hydrochloric acid (1 : 10), sulphuretted hydrogen being evolved.

Chrome Yellow.—Not dissolved, but changed to Chrome Orange by boiling with 2 per cent. sodium carbonate. Decomposed and dissolved upon boiling with dilute hydrochloric acid (1 : 10), a yellow solution containing chromic acid, which is taken up by wool, being obtained.

Chrome Orange.—Not dissolved upon boiling with 2 per cent. sodium carbonate, but immediately decomposed and dissolved by dilute hydrochloric acid (1 : 10).

Zinc Chrome.—Decolourised upon boiling with 2 per cent. sodium carbonate, giving a yellow solution of sodium chromate.

Cadmium Yellow.—Not dissolved by boiling with 2 per cent. sodium carbonate, but slowly dissolved upon boiling with dilute hydrochloric acid, sulphuretted hydrogen being liberated.

Orange and Red Lead.—Not changed upon boiling with 2 per cent. sodium carbonate, but dissolved by boiling with dilute hydrochloric acid (1 : 10).

Venetian Red, Ochre, Sienna, Umber.—Unaffected by 2 per cent. sodium carbonate and only very slightly attacked by boiling dilute hydrochloric acid (1 : 10).

Guignet Green (hydrated chromium oxide).—Insoluble in all the group reagents.

Vermillion.—Insoluble in all the group reagents.

Lamp Black, Ivory Black, Acetylene Black, etc.—Insoluble in all the group reagents.

Reagents.—The following reagents are employed. It is important that they should be used of the strength indicated.

Aqueous Sodium Carbonate (2 *per cent.*).—2 grams anhydrous sodium carbonate in 100 c.c. of water.

Aqueous Alcoholic Sodium Carbonate (1 *per cent.*).—50 c.c. of the previous solution mixed with 50 c.c. of alcohol.

Saline Caustic Soda.—10 c.c. of caustic soda lye of 35 to 40 per cent. NaHO and 100 c.c. of saturated salt solution.

Caustic Soda (5 *per cent.*).—5 grams of stick caustic soda in 100 c.c. of water.

Weak Formic Acid (1 : 100).—1 c.c. of commercial formic acid of 90 per cent. to 100 c.c. of distilled water.

Dilute Hydrochloric Acid (1 : 10).—10 c.c. of concentrated hydrochloric acid (30 per cent.) to 100 c.c. of water.

Tannin Solution.—10 grams of tannin and 10 grams of sodium acetate in 100 c.c. of water.

Hydrosulphite BASF.—Used solid.

Hydrosulphite AX.—Prepared as described on p. 58.

Persulphate.—Prepared as described on p. 59.

Stannous Chloride.—100 grams stannous chloride in 100 c.c. of concentrated hydrochloric acid and 50 c.c. of water.

Procedure.—*General.*—The analytical table which follows may be employed in the examination of a lake pigment either in the condition of lumps or powder, or when applied to paper or other surfaces in the form of a stain, lacquer, printing ink, lithographic ink, paint, distemper, etc. The oil or other medium with which the pigment is applied has usually but little effect upon the behaviour of the pigment with reagents. When the pigment is in powder form, filtration is necessary between each step in the separation, but when the pigment is adherent to a surface such as paper, wood, metal, etc., the extractions can generally be effected without the substratum leaving the surface, so that the extract can be simply poured off, leaving the residue ready to be subjected to the next reagent. This renders the work very expeditious and makes it possible to effect a complete analysis in a very short time. Even when the sample to be examined is in the form of powder or lumps it will be frequently found convenient first to apply it to paper by means of a suitable binding medium.

The extractions are usually performed upon about 0·1 gram pigment, or upon a piece of the stained or printed paper about one inch square or less. This is heated in a test-tube with about half an inch to one inch deep of the reagent. When more than one dyestuff is present and a separation of the constituents of the mixture has to be effected, it will be necessary to work with larger quantities than the above in order to obtain sufficient of the constituents for later tests.

Transference of Acid Dyestuffs to Wool.—In order to obtain a full shade suitable for subsequent tests, it is important that the extraction of the pigment should be effected with the mimimum quantity of liquid. Boiling for a few seconds with 2 per cent. sodium carbonate will usually suffice to dissolve the colour completely, but at longest a minute's boiling is enough. In a few cases in which the lake is not completely decomposed after boiling with aqueous sodium carbonate, this reagent may be replaced by aqueous-alcoholic sodium carbonate (1 per cent.). The coloured extract is poured off from the residue into another test-tube (or if necessary filtered), a small piece of white flannel about one inch square is added, the liquid rendered acid by addition of dilute hydrochloric acid (1 : 10) or dilute formic acid, and boiled for one or two minutes. The dyed wool is then removed and rinsed with water.

Transference of Basic Dyestuffs to Wool.—For this purpose the same method is used as for the transference of "basic" dyestuffs from cotton. This consists in liberating the free base from its combination with tannic, phosphoric, arsenious, or other acid by treatment with a boiling caustic soda solution which is saturated with salt in order to prevent the dye-base from dissolving. After rinsing with cold water to remove excess of caustic soda and salt, the dye-base can be dissolved in boiling water with or without addition of a little formic acid (1 : 100). From this solution, poured off or filtered from the residue, a piece of white flannel about one inch square is dyed by boiling for a minute or two. If, owing to the presence of an excess of formic acid, the wool does not take up the colour readily, dilute ammonia is added drop by drop until the excess of acid is nearly neutralised. In order to obtain a full shade the solution of the base should be effected in the minimum quantity of water. "Acid" dyestuffs if present must of course be completely removed prior to applying this test. Some aluminium lakes of "mordant" dyestuffs, such as Madder Red and Cochineal Carmine, are decomposed by saline caustic soda, giving a purple solution, but this is washed away upon rinsing with cold water and a coloured solution with formic acid is not obtained. Even if any colour passes into the acid solution it will not be precipitated by tannin.

Transference of Salt Dyestuffs to Cotton.—A small quantity of ammonium chloride is added to the colour extract obtained with 2 per cent. sodium carbonate, and the solution is boiled for about a minute with a piece of white mercerised cotton one inch square or less. The dyed cotton is afterwards boiled in plain water or in weak ammonia (1:100), in order to remove any ordinary "acid" dyestuff which may have been taken up.

Transference of Vat Dyestuffs to Cotton and Reduction of Azo Dyestuffs.—About 0·1 gram of the pigment or a piece of the coloured paper about one inch square is just covered with 2 per cent. sodium carbonate solution and heated to boiling. A little solid sodium Hydrosulphite BASF (say 0·1 gram or less) is added, together with a piece of white mercerised cotton about one inch square. The mixture is then boiled for about a minute and the cotton taken out and rinsed.

Reactions of the Dyestuffs upon Reduction and Reoxidation.—For further particulars regarding the prosecution of these tests the foregoing chapters on the detection of dyestuffs upon the wool and cotton fibres should be referred to.

Differentiation of Dyestuffs falling in the Same Class.—Having determined the class to which a dyestuff belongs, its further identification must be effected by making use of its reactions to various reagents, and by comparison of its shade and properties with products with which it is believed to correspond. For these purposes the published reactions of the dyed colouring-matters may be employed.[1] Use can also be made of the tables

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[1] See, for example, Heermann, *Koloristische und Textilchemische Untersuchungen.*

of solubilities and of individual reactions of a large number of dyestuff lakes compiled by George Zerr.[1] Where a suitable spectroscope is available, this instrument may be used with advantage for distinguishing the individual dyestuffs of a class or for supplementing the indications obtained by other methods.[2]

Notes and Special Reactions.

Section 1.—Pigment Chlorine 2G and Lithol Fast Yellow 2G dissolve in benzene rather slowly. The remaining members of this section are for the most part very easily soluble in benzene. Most of the colours of this section sublime on heating, those of the nitro class more easily than the azo compounds.

Sections 2 *and* 3.—The solubility in benzene of the colouring-matters of the vat class varies considerably. Some, such as Helio Fast Pink, are easily soluble, others, such as Indanthrene Yellow, are sparingly soluble. The members of this class must therefore be sought both in Sections 2 and 3 and in Section 18. The indigoid vat colours can be distinguished from those of the anthracene class by the paler colour of the leuco compounds of the former (generally yellow or colourless) either in alkaline solution or upon the cotton fibre, whilst those of the latter class are usually darker than the dyestuffs themselves. For example, Indanthrene Yellow is readily identified by the cotton being dyed a bright blue, which slowly changes to yellow on rinsing.

Section 3.—The dyestuffs of the stilbene series (Stilbene Yellows, Direct Yellows, Mikado Yellows, Mikado Oranges) are reduced more slowly than other azo dyestuffs.

Section 6.—The dyestuffs of the Eosine series (various brands of Eosine, Erythrosine, Phloxine, and Rose Bengal) may be distinguished and separated from "acid" dyestuffs containing sulphonic groups (such as Acid Eosines, Acid Phloxines, Acid Rhodamines, Azo Scarlets, Ponceaux, etc.) by the fact that their free colour acids are readily soluble in ether. To separate a mixture of an Eosine and a Ponceaux, for example, it is only necessary to acidify the aqueous solution with hydrochloric acid and to shake out with ether. On evaporating the yellow ethereal solution and neutralising with ammonia the Eosine is obtained. Such mixtures are frequently found in Geranium lakes. Rhodamine B, though usually regarded as a "basic" dyestuff, falls into this section, since its lakes are decomposed by sodium carbonate, doubtless by reason of the fact that it contains a carboxylic acid group. Unlike the true "acid" dyestuffs, however, it can be extracted from the alkaline solution by ether.

Section 9.—Some of these colours, notably Alkali Blues (largely used for

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[1] Zerr, *loc. cit.*

[2] Formánek u. Grandmougin, *Spektralanalytische Nachweis künstlicher organischen Farbstoffe* (Julius Springer, Berlin); for particulars of the constitution of the newer lake dyestuffs the reader is also referred to *Die neueren Farbstoffe der Pigmentfarben-Industrie*, von D. R. Staeble (Julius Springer, Berlin, 1910).

bronze blue printing inks), give nearly colourless solutions with 2 per cent. sodium carbonate. They are distinguished from Prussian Blue by the return of the colour on acidifying the filtered alkaline solution.

Section 10.—Naphthol Yellow S is characterised by passing through an orange stage on reduction. The azo dyestuffs of the pyrazolone series (Tartrazine, Fast Light Yellows, Normal Yellow, Pigment Chrome Yellows, Pyrazine Yellow, Sulphon Yellow, Radial Yellow, etc.) are characterised by the colourless solutions obtained upon reduction becoming violet when oxidised by air (Staeble). The dyestuffs of the Lithol Red and Lake Red group mostly dissolve in concentrated sulphuric acid, forming a violet solution which upon dilution with water and shaking with ether gives a pink ethereal layer. When not containing both a sulphonic and a carboxylic group they are soluble in acetone (Staeble).

Section 11.—Auramine is characterised by the production of a violet when its solution is reduced with zinc-dust and dilute hydrochloric acid and dried upon paper.

Section 12.—Safranine after reduction and oxidation does not return to its original shade but to a violet (formaldehyde derivative), which becomes red upon boiling with ammonia. The azine dyestuffs of the Safranine class dissolve in concentrated sulphuric acid giving a bright green colour, becoming blue and then red on adding water.

Section 13.—Most of the dyestuffs of this category dissolve in concentrated sulphuric acid giving a yellow or orange colour.

TABLE XXX.—SCHEME OF ANALYSIS OF LAKE PIGMENTS.

Boil with benzene for a quarter to one minute.

No.							
1.	Colour dissolves: **Neutral Dyestuff.** Boil fresh portion, or (when other dyestuffs are also present) the evaporated benzene extract, with 2 per cent. aqueous sodium carbonate, a little sodium hydrosulphite, and a small piece of white mercerised cotton.					Completely and permanently decolourised. Cotton remains uncoloured: **Nitro or Azo Class.**	LITHOL FAST YELLOW, PIGMENT CHLORIN 2G, HANSA YELLOWS, PIGMENT CHROME YELLOW L, LITHOL FAST ORANGE, TUSCALINE ORANGE, PIGMENT ORANGE R, AUTOL ORANGE, LITHOL FAST SCARLETS, AUTOL REDS, AUTOL BRILLIANT RED, PARATONER, HELIO FAST RED RL, PERMANENT REDS R, 4R, 2G, PIGMENT REDS B AND G, PIGMENT FAST RED HL, BRILLIANT LAKE RED R, SITARA FAST RED, HANSA RED B, PIGMENT BORDEAUX R AND N, EGLANTINE BBP, PIGMENT PURPLE A.
2.		Dissolves to a more or less coloured solution. Cotton is dyed: **Vat Dyestuff.**				Leuco compound is yellow **Indigoid Class.**	THIOINDIGO RED, THIOINDIGO SCARLET, HELINDONE ORANGE, HELINDONE SCARLET S, HELINDONE FAST SCARLET R, HELINDONE RED 3B, HELINDONE VIOLETS, CIBA VIOLETS R, B, AND 3B, HELINDONE BLUE 2B, CIBA BLUE 2BD, BRILLIANT INDIGOS, ALIZARINE INDIGO B.
3.						Leuco compound is red, brown, claret, or blue: **Anthracene Class.**	SIRIUS YELLOW, HELIO FAST YELLOWS GL, RL, 6GL, INDANTHRENE YELLOWS (FLAVANTHRENES), INDANTHRENE GOLD ORANGE, ALGOL YELLOW R, ALGOL RED 5G, ALGOL PINK TR, HELIO FAST PINK RL, ALGOL BRILLIANT VIOLETS R AND 2B.
4.						**Colour is undissolved and unchanged. Cotton remains uncoloured.**	CIBA LAKE RED B.
5.	**Colour undissolved.** Boil residue or fresh portion (in absence of colours of first section) with 2 per cent. aqueous sodium carbonate for one minute or less.	**The colour dissolves: Acid, Acid-mordant, or Salt Dyestuff.** Divide solution into two parts: (*a*) add ammonium chloride and boil with small piece of white mercerised cotton; (*b*) acidify with dilute hydrochloric or formic acid and boil with small piece of white wool.	The cotton is dyed: **Salt Dyestuff.** Boil the dyed cotton **with Hydrosulphite AX.**			**Decolourised. Colour** not restored **by air** or by **persulphate. Azo Class.**	STILBENE YELLOWS, DIRECT YELLOWS, MIKADO GOLDEN YELLOWS, PAPER YELLOW R AND 3G, CHLORAMINE ORANGES, MIKADO ORANGES, CHRYSOPHENINE, BENZO FAST SCARLET, BENZO FAST VIOLET, BENZO FAST BLUE, BENZAZURINE, DIANIL BLUES, PATENT DIANIL BLACK FFC, HELIO PURPURINE 10BL, BRILLIANT HELIO PURPURINE B, LITHOL BORDEAUX B AND R, LAKE BORDEAUX B.
6.						**Not decolourised: Thiazol Class.**	CHLORAMINE YELLOWS, PRIMAZINE ORANGE G.
7.			**The cotton is not dyed. The wool is dyed strongly: Acid or Acid-mordant Dyestuff.** Boil dyed wool with Hydrosulphite AX.			**Colour unaffected: Quinoline or Pyrone Class.**	QUINOLINE YELLOW O, EOSINES, ERYTHROSINES, PHLOXINES, ROSE BENGAL, ACID EOSINES, RHODAMINE B, ACID RHODAMINES.
8.						**Colour changed to yellow, orange, brown, etc. Original colour restored on oxidation: Anthracene Class.**	ALIZARINE RUBINOL 3GL, ANTHRAQUINONE VIOLET, HELIO FAST VIOLET AL, ALIZARINE HELIOTROPE R, ACID ALIZARINE BLUE 2B, ALIZARINE DIRECT VIOLET, ALIZARINE DIRECT BLUE B AND EB, HELIO FAST BLUE BL AND SL, CYANANTHROL, ANTHRAQUINONE GREEN GXN, ALIZARINE DIRECT GREEN G, ALIZARINE CYANINE GREEN 3G, ETC.
9.				**Decolourised.**		Colour returns on exposure to air: **Azines, Oxazines, or Thiazines.**	AZO CARMINE, NIGROSINES, INDULINES, CHROMOGLAUCINE, ETC.
10.						Colour does not return on exposure to air, but is restored by persulphate: **Triphenylmethane Class.**	ACID VIOLETS, FORMYL VIOLET, GUINEA VIOLET, SOLUBLE BLUES, OPAL BLUES, ALKALI BLUES, PATENT BLUES, KETONE BLUES, BRILLIANT ACID BLUE EG, BENZYL BLUE, ACID GREENS, NEPTUNE GREENS, GUINEA GREEN, ETC.
11.						Colour is not restored either by air or by persulphate: **Nitro, Nitroso, and Azo Class.**	NAPHTHOL YELLOW S, TARTRAZINE, FAST LIGHT YELLOWS, NORMAL YELLOWS, SULPHON YELLOW, RADIAL YELLOWS, PYRAZINE YELLOW, PIGMENT FAST YELLOWS, SATURN YELLOW, PERMANENT ORANGE R, FAST ORANGE O, BRILLIANT ORANGE G AND R, PAPER SCARLETS, PONCEAUX, BRILLIANT LAKE SCARLETS, PALATINE SCARLETS, LITHOL REDS R, 2G, 3G, 3B, LITHOL RUBINE B AND G, PERMANENT REDS 4B AND 6B, LAKE REDS C, D, AND P, PIGMENT SCARLETS G, R, 3B, PIGMENT RUBINE R, PIGMENT CARMINE 3B, PIGMENT VIOLET 2B, FAST LAKE BORDEAUX, BRILLIANT CARMINE, HELIO RED RM, HELIO ORANGES, HELIO BORDEAUX B, HELIO VIOLET, LAKE PURPLE 3B, NAPHTHOL GREEN B, ETC.
12.		**Colour undissolved. Heat residue to boiling for a few seconds with saline caustic soda, rinse with cold water, and boil with weak formic acid (1 : 100) and a small piece of white wool.**	Lake is decomposed and colour base dissolves in formic acid, giving solution which dyes wool and is precipitated by tannin and sodium acetate: **Basic Dyestuff.** Boil dyed wool with Hydrosulphite AX.			Colour unaffected: **Pyrone, Acridine, or Thiazol Class.**	THIOFLAVINE T, RHODULINE YELLOW AND ORANGE, AURAMINE, RHODAMINE 6G, ETC.
13.				**Decolourised.**		Colour returns on exposure to air: **Azines, Oxazines, or Thiazines.**	SAFRANINES, RHODULINE REDS AND VIOLETS, METHYLENE BLUES, FAST BLUES, NEW METHYLENE BLUES, CRESYL FAST VIOLET, ETC.
14.						Colour does not return on exposure to air, but is restored by persulphate: **Triphenylmethane Class.**	MAGENTA, NEW FUCHSINE, METHYL VIOLET, BENZYL VIOLET, VICTORIA BLUES, TURQUOISE BLUE, MALACHITE GREEN, BRILLIANT GREEN, FAST GREEN, SETOGLAUCINE, ETC.
15.						Colour is not restored either by air or by persulphate: **Azo Class.**	BISMARCK BROWN, VESUVINE, CHRYSOIDINE.
16.			**Lake not decomposed by saline caustic soda; or decomposed, but does not give a coloured solution in formic acid. Wool is not dyed.** Boil fresh sample (previously extracted with benzene and with 2 per cent. aqueous sodium carbonate when colours of earlier sections are present) with dilute hydrochloric acid (1 : 10).	Lake decomposed, often with complete change of colour: **Mordant Dyestuff.** Boil fresh sample with 5 per cent. caustic soda and zinc-dust or sodium hydrosulphite		Decolourised. Colour does not return on exposure to air: **Azo Class.**	ANTHRACENE RED, ETC.
17.						Coloured solution formed: **Anthraquinone or Pyrone Class.**	ALIZARINE REDS, ALIZARINE PURPLE, MADDER RED, ALIZARINE ORANGE, ALIZARINE BORDEAUX, BRILLIANT ALIZARINE BORDEAUX, ALIZARINE CYCLAMINE, ACID ALIZARINE BLUE 2B, ANTHRACENE BLUES WR AND WB, COCHINEAL CARMINE, ETC.
18				**Colour unaffected.** Boil residue or fresh sample with 5 per cent. caustic soda, sodium hydrosulphite, and a small piece of white mercerised cotton.	Colour dissolves and cotton is dyed: **Vat Dyestuff of Anthracene or Sulphur Class.** Apply stannous chloride test to the dyed cotton.	No hydrogen sulphide is evolved.	INDANTHRENE YELLOWS, CIBANONE ORANGE, INDANTHRENE BLUES, ALGOL BLUES, INDANTHRENE GREY.
19.						Hydrogen sulphide is evolved.	HYDRON BLUES, HYDRON VIOLET, INDANTHRENE OLIVE.
20.						Colour remains insoluble: some **Mineral Pigments.**	CARBON (LAMP BLACK, IVORY BLACK, ACETYLENE BLACK, ETC.), GUIGNET'S GREEN (CHROMIUM HYDRATE), VERMILION, VENETIAN RED, OCHRE, UMBER.

CHAPTER IX.

DETERMINATION OF THE CONSTITUTION OF AZO DYESTUFFS.

WITH the enormous multiplicity of azo combinations now obtainable and the large number of these compounds which at present come into commerce to be used in dyeing and lake manufacture, the complete elucidation of the constitution of a dyestuff of this class can often only be effected by breaking it up into simpler constituents the structure of which can be ascertained. Such a process is frequently made use of by the colour manufacturer who wishes to ascertain the composition, and consequently the mode of manufacture, of a newly introduced colouring-matter the properties of which do not correspond to known brands. For effecting this object two methods are available, viz.:

A. Reduction of the azo dyestuff to amido compounds and the isolation and identification of the latter:—

$$R'.N:N.R''.OH+2H_2 \qquad R'.NH_2+R''(OH)NH_2.$$

B. Treatment with cold fuming nitric acid, when a diazo salt and a nitrophenol are produced:—

$$R'.N:N.R''.OH+2HNO_3 \qquad R'.N_2.NO_3+R''(OH)(NO_2)$$

If the phenolic residue contains an easily replaceable hydrogen atom or sulphonic group, a further nitro group is simultaneously introduced.

The reduction process was first applied as a general method for the analysis of azo dyestuffs by Witt,[1] who recommended the use of a hydrochloric acid solution of stannous chloride as the reducing agent. Later, it was proposed by Grandmougin[2] to substitute for this reagent sodium hydrosulphite $Na_2S_2O_4$, which usually allows of a more ready isolation of the reduction products. It should be noted, however, that in employing this reagent for azo compounds

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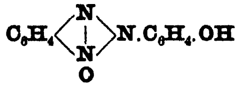
[1] Witt, *Ber.*, 1888, **21**, 3468.

[2] Grandmougin, *Ber.*, 1906, **39**, 2494, 3561, 3929; *J. prakt. Chem.*, 1907, p. 124.

derived from *o*-nitraniline, a normal reduction does not occur, but a derivative of benztriazol is produced; thus, for example, *o*-nitrobenzeneazophenol gives the compound



$$C_6H_4\left\langle\begin{matrix}N\\ |\\ \underset{\displaystyle O}{N}\end{matrix}\right\rangle N.C_6H_4.OH$$

a substance which crystallises in colourless needles of m.p. 232°.

The nitration process was first employed by Meldola and Morgan,[1] and subsequently elaborated by Schmidt.[2] Conclusions can be drawn as to the structure of the dyestuff, on the one hand by identification of the nitrophenol obtained, and on the other by examining the colour reactions given by the diazo salt with naphthols, etc. The method is particularly useful to supplement the indications of the reduction process in the case of azo compounds containing naphthol sulphonic acid residues. Thus, for example, azo derivatives of α-naphthol sulphonic acid 1 : 4 or of α-naphthol disulphonic acid 1 : 4 : 7 give respectively dinitro-α-naphthol,

$$C_{10}H_5(OH)(NO_2)_2[1:2:4],$$

and dinitro-α-naphthol sulphonic acid,

$$C_{10}H_4(OH)(NO_2)(SO_3H)[1:2:4:7],$$

which can be readily identified. The nitration method is also valuable in those cases in which, owing to the absence of a free amido or hydroxy group, the reduction of the azo compound does not occur smoothly. This is the case, for example, with dyestuffs of the type of sulphobenzeneazophenetol,

$$C_6H_4(SO_3H).N_2.C_6H_4.OC_2H_5.$$

Reduction Method. Procedure.—In selecting the method of procedure it is advisable to first try test-tube experiments with various reducing agents. Whilst sodium hydrosulphite and stannous chloride, more especially the former, first come into consideration, other reducing agents, such as zinc-dust and ammonia, zinc-dust and salt, glucose and caustic soda, sodium stannite, etc., are useful in special cases. Thus a very efficient method of reduction in certain instances is to add to the hot solution of the dyestuff a sufficiency of zinc-dust together with a small quantity of neutral sodium sulphite, and then to run in dilute hydrochloric acid slowly until

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[1] Meldola and Morgan, *Trans. Chem. Soc.*, 1889, **55**, 608.

[2] Schmidt, *Ber.*, 1905, **38**, 3201.

complete decolourisation ensues. Alkaline reducing agents are sometimes employed for effecting a partial reduction: thus the dyestuff known as Rosophenine 4B or St Denis Red,

$$N_2O\{C_6H_3(CH_3).N_2.C_{10}H_5(OH)(SO_3H)\}_2,$$

when submitted to reduction with glucose and caustic soda, or with sodium stannite, yields the parent base azoxytoluidine and amido-α-naphthol sulphonic acid 2 : 1 : 4; whilst upon treatment with stannous chloride or sodium hydrosulphite it is more completely broken up, giving *m*-tolylenediamine.

Reduction with Stannous Chloride.—A solution of stannous chloride is employed containing 40 grams of the crystallised salt in 100 c.c. of concentrated hydrochloric acid. The dyestuff (5 to 10 grams) is dissolved in the minimum quantity of boiling water (usually from ten to twenty times its weight), or in alcohol if insoluble in water, and the required quantity of stannous chloride is added in one portion to the nearly boiling solution. About 6 c.c. of the above stannous chloride solution (= 2 grams $SnCl_2$) are employed to each gram of pure colouring-matter present. If the dyestuff contains much salt and its solubility is thereby greatly reduced, it is advisable to purify it prior to reduction. Amido derivatives of second components such as amidonaphthols and their sulphonic acids, naphthylenediamine sulphonic acids, etc., usually either separate at once from the hot solution or upon cooling. In some cases they only separate after the solution has been saturated with salt or mixed with a large excess of concentrated hydrochloric acid. The amidonaphthol sulphonic acids, after filtering off and washing, are best purified by dissolving in a solution of neutral sodium sulphite and reprecipitating with hydrochloric acid. Sulphonic acids of 1 : 2 or 1 : 4 naphthylenediamines are obtained pure by dissolving in sodium acetate solution and reprecipitating with acetic acid.

The reduction liquid from which the above products have been separated is made alkaline and distilled, or is shaken with ether. If the first component of the dyestuff is a volatile base, such as aniline, toluidine, xylidine, chloraniline, anisidine, phenetidine, etc., this is readily isolated from the distillate and can be characterised by its boiling-point and other properties, and by the melting-point of its acetyl and benzoyl derivatives. If the first component is a non-volatile base, such as β-naphthylamine, benzidine, tolidine, dianisidine, etc., it can be extracted by ether from the alkaline solution and purified by distillation or by crystallisation of its hydrochloride or sulphate. *m*- or *p*-nitranilines and nitrotoluidines used as first components give rise to the corresponding diamines, which are not volatilised by steam but are extracted by ether from the alkaline solution. They can be purified by distillation and characterised by colour reactions, physical properties, and conversion into diacetyl compounds. If the first component is a sulphonated base, such as sulphanilic acid or toluidine sulphonic acid, it usually remains in great part dissolved in the excess of hydrochloric acid, and will crystallise out upon evaporation of the liquid. Sulphanilic acid is characterised by its crystalline form and by conversion into tribromaniline, m.p. 119°, upon treatment with bromine water, or by conversion into picric acid upon warming with nitric acid. Naphthionic acid is characterised by its sparing solubility and by conversion into dinitro-α-naphthol, m.p. 138°, upon warming with nitric acid.

Reduction with Sodium Hydrosulphite.—The dyestuff (10 grams) is dissolved in from 100 to 200 c.c. of boiling water, and solid sodium hydrosulphite (*e.g.* Hydrosulphite BASF) is added in small portions until complete decolourisation is effected (usually 10 to 20 grams are required). From the solution obtained, if necessary rendered slightly acid with hydrochloric acid, amidonaphthols, amidonaphthol sulphonic acids, naphthylenediamine sulphonic acids, amidosalicylic acid, amidopyrazolone sulphonic acids, etc., separate on cooling or after saturating the solution with common salt and allowing to stand. The precipitate is filtered off at the pump and washed with a little water. It can generally be purified by dissolving in neutral sodium sulphite and reprecipitating with hydrochloric acid.

For the isolation of the first component the filtrate from which the above products have separated is rendered alkaline with caustic soda and distilled with steam, when aniline, *o*- and *p*-toluidine, xylidines, chloranilines, anisidines, phenetidines, α-naphthylamine, etc., pass over. If the base is not volatile, the alkaline solution is extracted with ether, and the product purified by distillation (preferably *in vacuo*) or by crystallisation of its hydrochloride or sulphate. In those cases in which the sulphate of the base is sparingly soluble (benzidine, tolidine, dianisidine, diamidodiphenylamine, 1 : 4 naphthylenediamine) separation may be effected by adding sulphuric acid to the reduction liquid.

Sulphonated amines, such as sulphanilic acid, toluidine sulphonic acids, etc., usually remain in solution after reduction and are separated by acidifying the reduction liquid with hydrochloric acid.

When the azo compound is insoluble in water it is dissolved in alcohol, and a saturated aqueous solution of sodium hydrosulphite is added to the boiling liquid until complete decolourisation ensues. The solution is then distilled with steam, when alcohol passes over together with volatile bases (aniline, toluidine, etc.), whilst amido derivatives of second components (amido-β-naphthol, amidophenylmethylpyrazolone, etc.) separate out from the residue left in the flask. *m*- and *p*-diamines (derived from nitroamines employed as first components) can be obtained from the filtrate by extraction with ether.

Nitration Method.—The dyestuff (preferably freed from salt) is added slowly to from ten to twenty times its weight of red fuming nitric acid, which is kept cooled to 20° to 30°. After standing for about ten minutes, the colour of the solution will have changed to brownish yellow; the mixture is then poured upon chopped ice. According to the nature of the dyestuff, either the diazo compound or the nitrophenol, more usually the latter, may be sparingly soluble in water and therefore separate out. In other cases both products may be insoluble, in which event the nitrophenol is separated from the diazo compound by extracting the precipitate with alcohol, ether, or benzene. If both products remain dissolved, the nitrophenol, if unsulphonated, may be extracted from the liquid by ether, leaving the diazo compound in solution, or the latter may be removed by coupling with β-naphthol, leaving the nitrophenol in solution. The diazo compound is identified by coupling with β-naphthol or R-salt and reducing the product. The nitrophenol or nitrophenol ether is identified by its melting-point and other properties. Thus, dinitro-α-naphthol 1 : 2 : 4, which is obtained from azo derivatives of α-naphthol or of α-naphthol 2 or 4 sulphonic acids, melts at 138°, is sparingly soluble in water, and gives a characteristic calcium salt crystallising in orange leaflets. Dinitro-α-naphthol sulphonic acid 1 : 2 : 4 : 7 is soluble in water, but is precipitated as the orange-yellow potassium salt (Naphthol Yellow S) upon addition of potassium chloride. Dinitroanisol (obtained from azo compounds containing phenol as end component which is subsequently methylated) is insoluble in water and forms fine yellowish-white needles of m.p. 88°. Dinitrophenetol (obtained from the corresponding ethylated dyestuffs) crystallises in pale yellowish needles of m.p. 87°.

EXAMPLES.

I. Ponceau 2G.—

$$C_6H_5.N_2.C_{10}H_4(OH)(SO_3Na)_2.$$

Dissolve 10 grams of the dyestuff in 75 c.c. of boiling water, and to the hot solution add 11 grams of stannous chloride dissolved in 12·5 c.c. pure concentrated hydrochloric acid. When fully decolourised, filter quickly and add to the filtrate 75 c.c. of saturated salt solution. The crystalline magma formed is filtered off on the pump and well drained. The precipitate is then dissolved in a fairly strong solution of neutral sodium sulphite, filtered, and acidified with hydrochloric acid. The precipitate, which separates in fine colourless needles, is the acid sodium salt of amido-R-acid (amido-β-naphthol disulphonic acid 1 : 2 : 3 : 6). The filtrate from which the above product has separated is made alkaline with caustic soda and distilled with steam, when aniline passes over.

II. Ponceau 2R.—

$$C_6H_3(CH_3)_2.N_2.C_{10}H_4(OH)(SO_3Na)_2.$$

Dissolve 10 grams of the dyestuff in 100 c.c. of boiling water, and add to the hot solution 8 grams of solid sodium hydrosulphite. The solution obtained is filtered and the filtrate acidified until the brownish tint changes to yellow. On standing, the acid sodium salt of the amido-R-acid separates, and can be recrystallised from a small quantity of boiling water. The filtrate is rendered alkaline and distilled with steam, when a base passes over which is found to boil at 210° to 215° (commercial xylidine).

III. Crystal Ponceau.—

$$C_{10}H_7.N_2.C_{10}H_4(OH)(SO_3Na)_2.$$

Dissolve 10 grams of the dyestuff in the minimum amount of boiling water and reduce with sodium hydrosulphite as above. Upon distilling with steam, a solid base passes over which is characterised as α-naphthylamine by its melting-point, boiling-point, and by the melting-point of its acetyl derivative. The residue left in the flask (which must not be allowed to increase in volume) is filtered and acidified. On standing, the acid sodium salt of the amido-G-acid (amido-β-naphthol disulphonic acid 1 : 2 : 6 : 8) slowly separates, and can be purified by solution in sodium sulphite and reprecipitation by acid.

IV. Bordeaux S.—

$$C_{10}H_6(SO_3Na).N_2.C_{10}H_4(OH)(SO_3Na)_2.$$

Dissolve 10 grams of dyestuff in 100 c.c. of boiling water and add 3 grams of solid sodium hydrosulphite. Filter the decolourised solution and acidify hot with hydrochloric acid. Naphthionic acid separates at once and the filtrate deposits on standing the acid sodium salt of the amido-R-acid.

V. Orange II.—

$$C_6H_4(SO_3Na).N_2.C_{10}H_6.OH.$$

Dissolve 10 grams of the dyestuff in 75 c.c. of boiling water, add to the hot solution 10 grams of sodium hydrosulphite, and boil until a spot of the mixture on filter-paper shows a colourless rim. If the rim is yellow, more hydrosulphite must be added. The solution is now cooled, and the precipitated amido-β-naphthol is filtered off on the pump and washed with cold water. The mother liquors on acidification with hydrochloric acid deposit sulphanilic acid in crystals. For characterisation of the amido-β-naphthol it is converted into β-naphthoquinone. This is effected by mixing with 20 c.c. of dilute sulphuric acid (1 : 2), cooling with a little ice, and then adding a solution of 3 grams of sodium bichromate. The β-naphthoquinone which separates out is filtered off and washed with water.

VI. Alizarine Yellow G.—

$$C_6H_4(NO_2).N_2.C_6H_3(OH)CO_2H.$$

Dissolve 10 grams of the sodium salt in 100 c.c. of water, and reduce, boiling with 30 grams of sodium hydrosulphite. On cooling, amido-salicylic acid crystallises out. This is characterised by (*a*) conversion, on heating to about 280°, into *p*-amidophenol, which gives benzoquinone on acid oxidation; (*b*) formation of the acetyl compound, m.p. 218°. The mother liquor when rendered alkaline and extracted with ether yields *m*-phenylenediamine, identified by its colour reactions and by conversion into the diacetyl derivative, m.p. 191°.

VII. Benzoazurine G.—

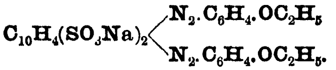
$$\begin{array}{l} C_6H_3(OCH_3).N_2.C_{10}H_5(OH)SO_3Na \\ \vert \\ C_6H_3(OCH_3).N_2.C_{10}H_5(OH)SO_3Na. \end{array}$$

Dissolve 10 grams of the dyestuff in 50 c.c. of boiling water containing 1 c.c. of caustic soda (40 per cent.), and to the boiling solution add gradually 5 grams of sodium hydrosulphite. The precipitate which separates on cooling is filtered off, dissolved in dilute hydrochloric acid, and the filtered solution reprecipitated with caustic soda. The base thus obtained, after recrystallisation from alcohol, has the melting-point 137° and gives the Zeisel test for methoxy groups, whilst its acetyl derivative melts at 231°. It is therefore dianisidine. The reduction fluid from which the dianisidine has been removed is acidified with hydrochloric acid, and the precipitate which separates upon standing is filtered off, and purified by dissolving in hot sodium sulphite solution, filtering, and reprecipitating with a little hydrochloric acid. The product is identified as amido-NW-acid,

$$C_{10}H_5(NH_2)(OH)SO_3H[2:1:4],$$

by oxidation with nitric acid to β-naphthoquinone sulphonic acid, which upon treatment with an aqueous solution of aniline gives the characteristic scarlet-red anilido-β-naphthoquinone, m.p. 252° to 253°.

VIII. Diamine Gold.—



$$C_{10}H_4(SO_3Na)_2\left\langle\begin{matrix}N_2.C_6H_4.OC_2H_5\\N_2.C_6H_4.OC_2H_5.\end{matrix}\right.$$

Dissolve 10 grams of the dyestuff in 100 c.c. of red fuming nitric acid, keeping the temperature at 20° to 30°. After standing for ten minutes pour upon chopped ice, filter off the precipitate on the pump, and wash free from acid with cold water. Extract the precipitate on the filter with cold absolute alcohol, and finally wash with a little ether. The alcoholic extract upon dilution with water gives a crystalline precipitate of dinitrophenetol,

$$C_6H_3(NO_2)_2OC_2H_5,$$

which is filtered off, washed with water, and recrystallised from benzene or ether. It melts at 87°. The diazo compound which is left on the filter after extraction with alcohol is coupled with an alkaline solution of β-naphthol, and the dyestuff is reduced with sodium hydrosulphite. After removing the amido-β-naphthol, the liquid on acidification gives a precipitate consisting of the diamidonaphthalene disulphonic acid,

$$C_{10}H_4(NH_2)_2(SO_3H)_2[1:5:3:7].$$

Characterisation of Reduction Products.

The identification of the first components of azo dyestuffs usually presents but little difficulty, as these generally consist of well-known amido compounds the properties of which are given in the literature. Thus aniline and its homologues, *o*- and *p*-anisidine *o*- and *p*-phenetidine, chloranilines, α- and β-naphthylamine, etc., are characterised by their melting- and boiling-points, and by the melting-points of their acetyl or benzoyl derivatives. Phenylene and tolylene *m*- and *p*-diamines are easily soluble in water, from which they are extracted with ether. They are identified by their melting-points, and by those of their diacetyl derivatives. Metadiamines give an orange-brown colouration with sodium nitrite and dilute acetic acid. Paradiamines yield a bright blue colouration (indamine) upon adding a few drops of chromic acid to a dilute aqueous solution containing an excess of aniline hydrochloride. Benzidine, tolidine, and dianisidine are insoluble in water and form sparingly soluble sulphates, the most insoluble being that of benzidine. These bases are characterised by their melting-points and by the melting-points of their acetyl derivatives. Sulphonic acids of aniline, of toluidines, and of α- and β-naphthylamines, are characterised by their crystalline form, solubility in water, and by their hydrolysis to amines upon fusion with caustic soda (*p*-sulphanilic acid), or on treatment in aqueous solution with sodium amalgam (β-naphthylamine sulphonic acids), or by heating to 180° with 75 per cent. sulphuric acid (naphthionic acid). *p*-Sulphanilic acid is distinguished from *m*-sulphanilic acid by the formation of benzoquinone on oxidation with chromic acid, and of tribromaniline, m.p. 119°, on treatment with bromine water. α-Naphthylamine sulphonic acids 1 : 2 and 1 : 4 are distinguished from the 1 : 5, 1 : 6, 1 : 7, and 1 : 8 isomers by the production of dinitro-α-naphthol 1 : 2 : 4 upon heating with concentrated nitric acid and then pouring into water. The precipitated dinitronaphthol can be purified by conversion into the calcium salt.

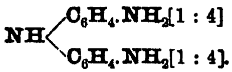
The identification of the final (or middle) components of an azo dyestuff presents greater difficulties than that of the first components, by reason of the fact that they are obtained upon reduction not as such but in the form of their amido compounds. In the following list will be found enumerated the most important of these amido compounds, together with a few of the less familiar first components, and the reactions by which they are best characterised.

p-Amidodiphenylamine.—

$$C_6H_5.NH.C_6H_4.NH_2[1:4].$$

Plates. M.p. 75° (from light petroleum). Sparingly soluble in water. Sulphate sparingly soluble in water. On oxidation in acid aqueous solution with hydrogen peroxide in presence of a trace of ferrous sulphate, a voluminous indigo blue precipitate of Willstätter's imide, $C_6H_5.N:C_6H_4:N.C_6H_4.NH.C_6H_4.NH_2$, is formed.

Di-p-amidodiphenylamine.—



$$NH\begin{cases} C_6H_4.NH_2[1:4] \\ C_6H_4.NH_2[1:4]. \end{cases}$$

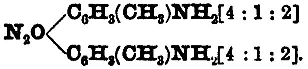
Plates (from water). M.p. 158°. Sulphate sparingly soluble in water. Oxidation of its salts in cold dilute aqueous solution with chromic acid gives a bright blue indamine. Diacetyl derivative, needles, m.p. 239°.

Dichlorbenzidine.—

$$\begin{array}{l} C_6H_3Cl.NH_2[1:2:4] \\ C_6H_3Cl.NH_2[1:2:4]. \end{array}$$

Needles. M.p. 133.°

Azoxytoluidine.—



$$N_2O\begin{cases} C_6H_3(CH_3)NH_2[4:1:2] \\ C_6H_3(CH_3)NH_2[4:1:2]. \end{cases}$$

Yellow needles or orange prisms. M.p. 168°. Best isolated by means of its hydrochloride, which is sparingly soluble in salt solution or in excess of hydrochloric acid. Diacetyl derivative, m.p. 290°.

p-Naphthylenediamine.—

$$C_{10}H_6(NH_2)_2[1:4].$$

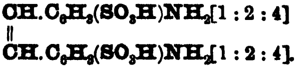
Separated as the sparingly soluble sulphate by addition of sulphuric acid to the reduction liquor, basified with caustic soda and distilled *in vacuo.* M.p. 120°. Gives a green fluorescent ethereal solution when shaken with ether in presence of alkalies.

Amidosalicylic Acid.—

$$C_6H_3(OH)(NH_2)CO_2H[1:4:2].$$

Sparingly soluble needles. Decomposes at about 280°, evolving carbonic acid and giving *p*-amidophenol. Its hydrochloride is sparingly soluble in excess of hydrochloric acid. The acetyl compound is prepared by dissolving the acid (1·5 grams) in sufficient caustic potash (0·6 gram in 10 c.c. of water) and shaking vigorously with acetic anhydride (1 gram). The acetyl compound which separates is recrystallised from water and melts at 218°.

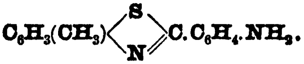
Diamidostilbene Disulphonic Acid.—



$$\begin{array}{l} CH.C_6H_3(SO_3H)NH_2[1:2:4] \\ \| \\ CH.C_6H_3(SO_3H)NH_2[1:2:4]. \end{array}$$

Sparingly soluble crystalline precipitate of ochreous colour. Easily soluble in alkalies. On diazotisation it yields a very sparingly soluble tetrazo compound as a microcrystalline powder which gives a violet dyestuff on combination with R-salt. A cold dilute solution of diamidostilbene disulphonic acid in aqueous soda is readily oxidised by potassium permanganate to *p*-amidobenzaldehyde sulphonic acid, $C_6H_3(NH_2)(SO_3H)CHO[4:2:1]$, which on treatment with phenylhydrazine yields a deeply coloured hydrazone.

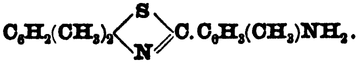
Dehydrothiotoluidine.—



$$C_6H_3(CH_3)\left\langle\begin{matrix}S\\N\end{matrix}\right\rangle C.C_6H_4.NH_2.$$

Glistening yellowish needles (from amyl alcohol). M.p. 191°. B.p. 434°. Insoluble in water and sparingly soluble in alcohol. Its salts are sparingly soluble and decomposed by water. Solutions fluoresce violet-blue or green. Acetyl derivative, m.p. 227°.

Dehydrothioxylidine.—



$$C_6H_2(CH_3)_2\left\langle\begin{matrix}S\\N\end{matrix}\right\rangle C.C_6H_3(CH_3)NH_2.$$

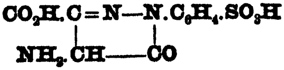
Similar to preceding, but more soluble in alcohol. M.p. 107°. Very high boiling-point. Acetyl derivative, m.p. 227°.

Dehydrothiotoluidine Sulphonic Acid.—

$$C_6H_3(CH_3)\left\langle\begin{matrix}S\\N\end{matrix}\right\rangle C.C_6H_3(NH_2)(SO_3H).$$

Yellow precipitate insoluble in water. Its ammonium salt crystallises from water in sparingly soluble yellowish-white leaflets. It gives an insoluble yellow diazo compound. The salts have a blue fluorescence.

Sulphophenylamidopyrazolone Carboxylic Acid.—



$$\begin{array}{l} CO_2H.C=N—N.C_6H_4.SO_3H \\ \quad\;\; | \qquad\quad | \\ NH_2.CH——CO \end{array}$$

Small needles, nearly insoluble in cold water or alcohol. The alkaline solution on exposure to air becomes reddish violet. A similar reaction is exhibited by other amido-pyrazolones and appears to be characteristic of these compounds.

Amido-β-naphthol.—

$C_{10}H_6(NH_2)(OH)[1 \cdot 2]$.

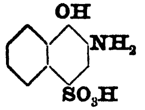
Quadratic prisms (from ether). Nearly insoluble in water. Best characterised by oxidation to β-naphthoquinone by mixing the crude product obtained from 10 grams of dyestuff with 20 c.c. of dilute sulphuric acid (1 : 2), cooling with ice, and adding 3 grams of sodium bichromate dissolved in a little water. The naphthoquinone separates out at once, and is washed with water and dried.

Amido-β-oxynaphthoic Acid.—

$C_{10}H_5(NH_2)(OH)(CO_2H)[1 : 2 : 3]$.

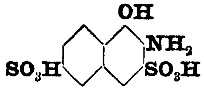
Yellow prisms (from hot alcohol). Decomposes without melting at 205°. On boiling with dilute sulphuric acid or hydrochloric acid it is converted into dioxynaphthoic acid of m.p. 220°.

Amido-NW-acid.—



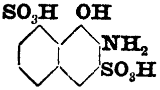
Not very soluble in cold water. The ammoniacal solution on filter-paper becomes rapidly green on exposure to air, finally assuming a deep myrtle colour which gives a bright terra-cotta spot with concentrated hydrochloric acid. The green colour changes to violet and then to red on warming, but returns to green on exposure to ammonia vapour. The solution in sodium acetate becomes violet on exposure to air. No characteristic reaction with ferric chloride. Nitrous acid gives a red solution, becoming orange. The acid is best characterised by oxidation to the very reactive β-naphthoquinone sulphonic acid. This is readily effected by dissolving the amido acid in three times its weight of nitric acid (specific gravity 1·4), warming gently, and as soon as the reaction is complete pouring into saturated salt solution. The sodium salt of the quinone sulphonic acid, $C_{10}H_5O_2(SO_3Na)$, separates in golden-yellow needles, and condenses very easily with amines, giving, for example, with an aqueous solution of aniline the bright red anilido-β-naphthoquinone, $C_{10}H_5O_2(NHC_6H_5)$. This crystallises from hot alcohol in glistening golden needles. M.p. about 253°.

Amido-Freund's Acid.—



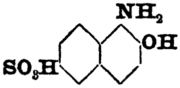
Rather sparingly soluble in water. The ammoniacal solution exposed to air on filter-paper is greenish yellow, becoming dull green, and then giving a pink spot with concentrated hydrochloric acid. No colouration with ferric chloride.

Amido-ε-acid.—



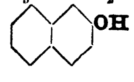
Crystallises from water in long colourless needles. Not very soluble cold. The ammoniacal solution on filter-paper becomes greenish yellow, and then gives a pale pink spot with hydrochloric acid. No reaction with ferric chloride or with nitrous acid.

Amido-Schaeffer Acid.—



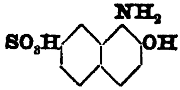
White crystalline powder. Easily soluble in hot water, sparingly in cold. The ammoniacal solution on filter-paper turns brown, the brown colour giving a lilac spot with ·concentrated hydrochloric acid which at once becomes pink. No reaction with ferric chloride or with nitrous acid. In presence of sodium acetate it gives characteristic reactions with diazo compounds; thus with tetrazostilbene disulphonic acid a reddish-violet colouring-matter is formed which becomes bright blue on adding hydrochloric acid. It does not react with nitrosodimethylaniline hydrochloride.

Amido-Bayer Acid.—



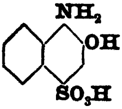
Sparingly soluble even in boiling water. Dissolves with difficulty in a solution of sodium acetate, and separates out again on cooling. The ammoniacal solution on filter-paper develops a greenish-yellow colour, deepening to reddish brown, and on spotting with concentrated hydrochloric acid the brown colour is discharged, leaving a bright orange rim. Ferric chloride gives a yellow colouration. No reaction with diazo compounds. On heating with nitrosodimethylaniline hydrochloride in 50 per cent. acetic acid solution, a characteristic violet dyestuff is produced.

Amido-δ-acid.—



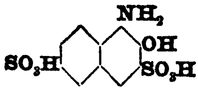
Small needles. Very similar in properties to the amido-Schaeffer acid, but more insoluble in water and less reactive. It does not react with nitrosodimethylaniline, but gives colouring-matters with diazo compounds, though less readily than the amido-Schaeffer acid.

Amido-β-naphthol Sulphonic Acid 1 : 2 : 4.—



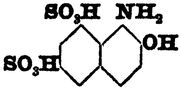
White crystalline powder. Insoluble in water. Is best characterised by conversion into the very reactive β-naphthoquinone sulphonic acid, $C_{10}H_5O_2(SO_3H)$[1 : 2 : 4] (see above). This is readily effected by stirring into one and a half times its weight of dilute nitric acid (20 per cent.), dissolving the paste obtained in water and adding a concentrated solution of potassium chloride, when the sparingly soluble potassium salt of the quinone sulphonic acid separates in golden-yellow needles. The latter deflagrates on heating between 170° and 175°, and when treated with an aqueous solution of aniline gives the above mentioned anilido-β-naphthoquinone, $C_{10}H_5O_2(NHC_6H_5)$, which crystallises from hot alcohol in glistening golden needles, melting with decomposition at about 253°.

Amido-R-acid.—



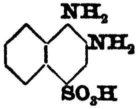
Easily soluble in water. On adding sodium chloride to the reduction fluid it separates as the acid sodium salt in white silky needles. The ammoniacal solution on filter-paper becomes greenish yellow, which gives a pale pink spot with concentrated hydrochloric acid. No reaction with ferric chloride. It does not give colourations either with diazo compounds or with nitrosodimethylaniline.

Amido-G-acid.—

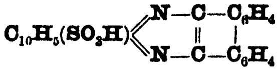


Easily soluble in water. On adding sodium chloride to the reduction liquid the acid sodium salt separates in microscopic prisms. The ammoniacal solution on filter-paper becomes greenish yellow, and finally reddish brown, the brown colour giving an orange-scarlet spot with hydrochloric acid. No reaction with ferric chloride. Though very similar to the preceding acids, it is more stable and less oxidisable.

Amido-naphthionic Acid.—



Sparingly soluble in water. The ammoniacal solution is only oxidised very slowly by air, becoming pale greenish brown, which is changed to a pale pink by concentrated hydrochloric acid. Ferric chloride in small amount gives a dirty green colouration, becoming rapidly brownish black; with an excess of ferric chloride it becomes dull green, and on standing or warming, bright grass green with a green precipitate. It is best characterised by condensation with phenanthraquinone to the crystalline quinoxaline sulphonic acid,



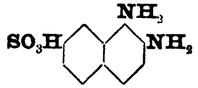
$$C_{10}H_5(SO_3H)\left\langle\begin{array}{l} N-C-C_6H_4 \\ \qquad \| \quad\;\; | \\ N-C-C_6H_4 \end{array}\right.$$

which gives a bluish-violet solution in concentrated sulphuric acid. This condensation is effected by mixing the boiling solution, acidified with acetic acid, with a solution containing the equivalent quantity of phenanthraquinone dissolved in the requisite amount of sodium bisulphite solution, and to which is also added an excess of sodium acetate. The quinoxaline separates almost immediately in fine lemon-yellow needles.

Amido-Bronner Acid.—

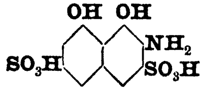
Fine pointed or flat needles. Very sparingly soluble in water. The ammoniacal solution oxidises in air very slowly, finally developing a brownish-pink colouration, which is changed to red and then slowly decolourised when spotted with concentrated hydrochloric acid. Ferric chloride gives a yellow colouration, rapidly becoming deep bluish green. It condenses with phenanthraquinone, giving a crystalline yellow quinoxaline which is distinguished from that obtained from the preceding isomer by dissolving in concentrated sulphuric acid with a redder shade of violet.

Amido-F-acid.—



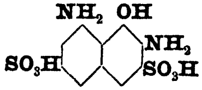
More soluble than the two preceding acids. It is indistinguishable in general properties from the amido-Bronner acid, and gives a quinoxaline sulphonic acid which also dissolves in concentrated sulphuric acid giving a reddish-violet colour. It can be distinguished, however, by the behaviour of the hydroxyazine obtained upon fusing a little of the quinoxaline sulphonic acid with caustic soda and precipitating with dilute hydrochloric acid. The hydroxyazine from the F-acid gives a violet solution in concentrated sulphuric acid which becomes brownish red on dilution; that from the Bronner acid gives a pure blue, changed to cherry red on dilution.

Amido-chromotropic Acid.—



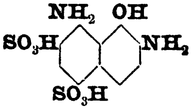
Easily soluble in water. The ammoniacal solution turns orange on exposure to air. The orange colour gives a yellow spot with concentrated hydrochloric acid, which fades on drying. The solution in sodium acetate is scarcely oxidised by air. Excess of ferric chloride produces a brownish-red colouration.

Amido-H-acid.—



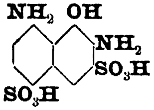
Easily soluble in water. The ammoniacal solution on filter-paper becomes bright orange in air. The orange colour gives with concentrated hydrochloric acid a bright blue spot, quickly becoming more violet with a magenta-coloured rim. The sodium acetate solution oxidises in air more slowly than the ammoniacal. Ferric chloride added to the dilute aqueous solution gives a bluish-violet colouration, rapidly becoming magenta red.

Amido-2S-acid.—



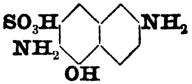
Easily soluble in water. The ammoniacal solution on filter-paper behaves very similarly to that of the amido-H-acid. The reaction with ferric chloride is also the same. The sodium acetate solution becomes dull green on exposure to air, changing later to pink. The green colour gives a greyish-blue spot with concentrated hydrochloric acid.

Amido-K-acid.—



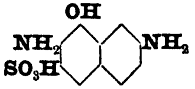
Reactions very similar to the amido-H-acid.

Amido-J-acid.—



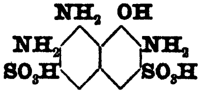
Sparingly soluble in water. The hot aqueous solution has a blue fluorescence, and dilute alkaline solutions (in presence of sodium hydrosulphite) have a bright green fluorescence. The ammoniacal solution exposed to air on filter-paper is at first greenish yellow, rapidly becoming brown. The brown colour gives with concentrated hydrochloric acid a green spot, which almost immediately becomes pink with a green rim. With dilute hydrochloric acid the brown colour gives a bright green spot, becoming duller. Added to a very dilute aqueous suspension of the acid, a drop of ferric chloride gives at first a dull green colour, which rapidly becomes dull violet, then bluish red, and finally brownish red. In aqueous suspension the acid can be diazotised and coupled with β-naphthol.

Amido-γ-acid.—



Sparingly soluble in water. The ammoniacal solution exposed to air on filter-paper rapidly becomes brown, and the brown colour gives a dull violet spot with concentrated hydrochloric acid. Ferric chloride gives a green colour, rapidly becoming violet. Nitrous acid gives a deep brown solution.

Diamido-H-acid.—



Colourless crystalline powder which rapidly becomes bright blue on exposure to air. The aqueous solution also rapidly becomes bright blue. The ammoniacal solution on filter-paper quickly becomes deep bluish violet, and finally greyish black. With concentrated hydrochloric acid the violet colour gives a bright bluish-green spot and the grey colour a brilliant green. Ferric chloride gives a thick blue precipitate. Nitrous acid also gives the same reaction. The blue precipitate is soluble in dilute caustic soda, giving a bright bluish-red solution.

KEY TO TRADE DESIGNATIONS.

Trade Name of Group of Products.	Dyeing Class.	Manufacturer.
Acid Alizarine	Acid Chrome	Meister, Lucius.
Acid Anthracene	Acid Chrome	Bayer & Co.
Acid Chrome	Acid Chrome	Bayer & Co.
Acidol	Acid	Weiler-ter-Meer.
Acidol Chromate	Acid Chrome	Weiler-ter-Meer.
Acridine	Basic	Leonhardt & Co.
Aetz	Acid (discharge)	Soc. Chem. Ind., Basle.
Algole	Vat	Bayer & Co.
Alizadine	Acid Chrome	British Dyestuffs Corporation.
Alizarine	Mordant, Chrome, and (Fast Acid)	Various.
Alizarine Azo	Acid Chrome	Durand, Huguenin & Co.
Alizarol	Acid Chrome	National Aniline Co.
Alkali	Salt	Dahl & Co.
Alphanol	Acid	L. Cassella & Co.
Amacid	Acid	American Aniline Products Co.
Amanil	Salt	American Aniline Products Co.
Amido	Acid	Meister, Lucius.
Aminine	Salt	F. à Brassard & Co.
Anachrome	Acid Chrome	F. à Brassard & Co.
Anthra Chromate	Acid Chrome	Leonhardt & Co.
Anthra Chrome	Acid Chrome	Leonhardt & Co.
Anthracene Acid	Acid Chrome	Cassella & Co.
Anthracene Chromate	Acid Chrome	Cassella & Co.
Anthracene Chrome	Acid Chrome	Cassella & Co.
Anthracyanine	Acid	Bayer & Co.
Anthracyl Chrome	Acid Chrome	Dahl & Co.
Anthranol	Acid Chrome	Dahl & Co.
Anthraquinone	Acid	Badische Aniline Co.
Auronal	Sulphur	Weiler-ter-Meer.
Auto Chrome	Acid Chrome	Meister, Lucius.
Autogene	Sulphur	A. Poirrier. (St. Denis).
Autol	Pigment	Badische Aniline Co.
Azidine	Salt	Carl Jäger & Co.
Azo	Acid	Various.
Azo Acid	Acid	Various.
Azo Alizarine	Acid Chrome	Durand, Huguenin & Co.
Azophor	Coupled	Meister, Lucius.
Benzamine	Salt	Dahl & Co.
Benzo	Salt	Bayer & Co.
Benzo Chrome	Salt (chromed)	Bayer & Co.
Benzo Fast	Salt	Bayer & Co.
Benzoform	Salt (formaldehyde)	Bayer & Co.
Benzoin	Salt	Beyer & Kegel.
Benzo Light	Salt (light fast)	Bayer & Co.
Benzonitrol	Coupled salt	Bayer & Co.
Benzyl	Acid	Soc. Chem. Ind., Basle.
Biebrich	Acid	Kalle & Co.
Brilliant Alizarine	Chrome	Bayer & Co.
Brilliant Benzo	Salt	Bayer & Co.

KEY TO TRADE DESIGNATIONS—*continued.*

Trade Name of Group of Products.	Dyeing Class.	Manufacturer.
Brilliant Dianil	Salt	Meister, Lucius.
Brilliant Fat	Oil, soluble	Soc. Chem. Ind., Basle.
Buffalo	Acid	National Aniline Co.
Caledon	Vat	Scottish Dyes.
Cerasine	Spirit and Oil, soluble	L. Cassella & Co.
Ceres	Dyes for lakes	Bayer & Co.
Chicago	Salt	Berlin Aniline Co.
Chloramine	Salt	Bayer & Co., Sandoz Chem. Co.
Chloranthrene	Vat	British Dyestuffs Corporation.
Chlorantine	Salt	Soc. Chem. Ind., Basle.
Chlorazol	Salt	British Dyestuffs Corporation.
Chromanthrene	Chrome	British Dyestuffs Corporation.
Chromanil	Salt (chromed)	Berlin Aniline Co.
Chrome Fast	Acid Chrome	Soc. Chem. Ind., Basle.
Chromoxan	Acid Chrome	Bayer & Co.
Ciba	Vat	Soc. Chem. Ind., Basle.
Cibanone	Vat	Soc. Chem. Ind., Basle.
Columbia	Salt	Berlin Aniline Co.
Congo	Salt	Berlin Aniline Co.
Coomassie	Acid	British Dyestuffs Corporation.
Cotton	Salt	Various.
Cross Dye	Sulphur	British Dyestuffs Corporation.
Crumpsall	Acid	British Dyestuffs Corporation.
Cyananthrol	Acid	Badische Aniline Co.
Diadem Chrome	Acid Chrome	L. B. Holliday & Co.
Diamine	Salt	L. Cassella & Co.
Diamine Nitrazol	Coupled Salt	L. Cassella & Co.
Diamond	Acid Chrome	Bayer & Co.
Dianil	Salt	Meister, Lucius.
Dianil Fast	Salt	Meister, Lucius.
Dianol	Salt	British Dyestuffs Corporation.
Diazanil	Developed Salt	Meister, Lucius.
Diazine	Basic	Kalle & Co.
Diazo	Developed Salt	Bayer & Co.
Diazo Light	Developed Salt	Bayer & Co.
Diazogen	Developed Salt	Jäger & Co.
Diphenyl	Salt	Geigy & Co.
Direct	Salt	Various.
Discharge	Acid (dischargeable)	Soc. Chem. Ind., Basle.
Domingo	Acid	Leonhardt & Co.
Domingo Alizarine	Acid Chrome	Leonhardt & Co.
Domingo Chrome	Acid Chrome	Leonhardt & Co.
Duatol	Dyes for Union Goods	L. Cassella & Co.
Duranthrene	Vat	British Dyestuffs Corporation.
Durindone	Vat	British Dyestuffs Corporation.
Durrol	Fur Dyes	L. Cassella & Co.
Eboli	Salt	Leonhardt & Co.
Eclipse	Sulphur	Geigy & Co.
Era Chrome	Acid Chrome	British Dyestuffs Corporation.
Erganone	Chrome, Printing	Badische Aniline Co.
Erie	Salt	National Aniline Co.
Erio	Acid	Geigy & Co.

KEY TO TRADE DESIGNATIONS—*continued.*

Trade Name of Group of Products.	Dyeing Class.	Manufacturer.
Erio Chromal	Acid Chrome	Geigy & Co.
Erio Chrome	Acid Chrome	Geigy & Co.
Erweco-Alizarine	Mordant	R. Wedekind & Co.
Formal	Salt (formaldehyde)	Geigy & Co.
Gallanil	Acid Chrome	Durand, Huguenin & Co.
Gallo	Chrome, Printing	Bayer & Co.
Glycine	Salt	Kinzlberger & Co.
Graphitol	Lake Colours	Griesheim-Elektron.
Guinea	Acid	Berlin Aniline Co.
Half-Wool	Dyes for Union Goods	Various.
Hansa	Lake Colours	Meister, Lucius.
Helindone	Vat	Meister, Lucius.
Helio	Lake Colours	Bayer & Co.
Hessian	Salt	Leonhardt & Co.
Hydranthrene	Vat	L. B. Holliday & Co.
Hydron	Vat	L. Cassella & Co.
Hydrosulphon	Sulphur	F. à Brassard & Co.
Immedial	Sulphur	L. Cassella & Co.
Indanthrene	Vat	Badische Aniline Co.
Janus	Basic	Meister, Lucius.
Kashmir	Acid	Bayer & Co.
Katigen	Sulphur	Bayer & Co.
Kiton	Acid	Soc. Chem. Ind., Basle.
Kyrogene	Sulphur	Badische Aniline Co.
Lanacyl	Acid	L. Cassella & Co.
Lanasol	Acid Chrome	Soc. Chem. Ind., Basle.
Leucol	Vat	Bayer & Co.
Lissamine	Acid	British Dyestuffs Corporation.
Lithol	Lake Colours	Badische Aniline Co.
Mercerol	Acid	British Dyestuffs Corporation.
Meta Chrome	Acid Chrome	Berlin Aniline Co.
Methylene	Basic	Meister, Lucius.
Mikado	Salt	Leonhardt & Co.
Milling	Acid	Various.
Modern	Printing Colours	Durand, Huguenin & Co.
Monochrome	Acid Chrome	Bayer & Co.
Naka	Fur Dyes	Meister, Lucius.
Naphthamine	Salt	Kalle & Co.
Naphthol	Acid	Various.
Naphthylamine	Acid	Various.
Neoform	Salt (formaldehyde)	Soc. Chem. Ind., Basle.
Neptune	Acid	Badische Aniline Co.
Niagara	Coupled Salt	National Aniline Co.
Normal	Acid	Meister, Lucius.

KEY TO TRADE DESIGNATIONS—*continued.*

Trade Name of Group of Products.	Dyeing Class.	Manufacturer.
Oil	Oil, soluble	Various.
Omega Chrome	Acid Chrome	Sandoz Chemical Co.
Ortho	Acid	Berlin Aniline Co.
Oxamine	Salt	Badische Aniline Co.
Oxy Chrome	Acid Chrome	Griesheim-Elektron
Oxy Diamine	Salt	L. Cassella & Co.
Palatine	Acid	Badische Aniline Co.
Palatine Chrome	Acid Chrome	Badische Aniline Co.
Para	Coupled Salt	Bayer & Co.
Paramine	Salt	L. B. Holliday & Co.
Paranil	Coupled Salt	Berlin Aniline Co.
Paranol	Salt	U.S. Colour & Chemical Co.
Paraphor	Coupled Salt	Meister, Lucius.
Permanent	Lake Colours	Berlin Aniline Co.
Phenochrome	Chrome, Printing	Kalle & Co.
Phenyl	Acid	Cie. Francaise de St.-Clair-du-Rhone.
Pigment	Lake Colours	Meister, Lucius.
Pluto	Salt	Bayer & Co.
Plutoform	Salt	Bayer & Co.
Polar	Acid	Geigy & Co.
Polyphenyl	Salt	Geigy & Co.
Pontacyl	Acid	Du Pont de Nemours.
Pontamine	Salt	Du Pont de Nemours.
Pontochrome	Acid Chrome	Du Pont de Nemours.
Primazine	Lake Colours	Badische Aniline Co.
Pyramine	Salt	Badische Aniline Co.
Pyrazol	Salt	Sandoz Chemical Co.
Pyrogene	Sulphur	Soc. Chem. Ind., Basle.
Pyrol	Sulphur	Leonhardt & Co.
Pyronal	Oil, soluble	Dahl.
Radial	Acid	Badische Aniline Co.
Renol	Salt	Weiler-ter-Meer.
Rhoduline	Basic	Bayer & Co
Rosanthrene	Salt	Soc. Chem. Ind., Basle.
St. Denis	Salt	A. Poirrier. (St. Denis).
Salicine	Acid Chrome	Kalle & Co.
Serichrome	Acid Chrome	National Aniline Co.
Seto	Acid	Geigy & Co.
Sita	Lake Colours	Weiler-ter-Meer.
Solochrome	Chrome	British Dyestuffs Corporation.
Stilbene	Salt	Various.
Sulphanil	Salt	Kalle & Co.
Sulphogene	Sulphur	Du Pont de Nemours, Soc. Chem. Ind., Basle.
Sulphon	Acid and Salt	Bayer & Co.
Sulphon Acid	Acid	Bayer & Co.
Sulphur	Sulphur	Berlin Aniline; National Aniline Co.
Sulphurol	Sulphur	Dahl & Co.
Sultan	Salt	British Dyestuffs Corporation.
Supramine	Acid	Bayer & Co.
Superchrome	Acid Chrome	National Aniline Co.

KEY TO TRADE DESIGNATIONS—*continued.*

Trade Name of Group of Products.	Dyeing Class.	Manufacturer.
Tannate	Basic	Dahl & Co.
Thiazine	Salt	Bayer & Co.
Thio Indigo	Vat	Kalle & Co.
Thiogene	Sulphur	Meister, Lucius.
Thion	Sulphur	Kalle & Co.
Thional	Sulphur	Sandoz Chemical Co.
Thionol	Sulphur	British Dyestuffs Corporation.
Thionone	Sulphur	L. B. Holliday & Co.
Thioxine	Sulphur	Griesheim-Elektron.
Titan	Salt	British Dyestuffs Corporation.
Toluylene	Salt	Griesheim-Elektron.
Triatol	Dyes for Union Goods.	Gustav Dörr & Co.
Triazol	Salt	Griesheim-Elektron.
Trisulphon	Salt	Soc. Chem. Ind., Basle.
Ultra	Chrome	Sandoz Chemical Co.
Ursol	Fur Dyes	Berlin Aniline Co.
Victoria	Acid	Various.
Vidal	Sulphur	A. Poirrier. (St. Denis).
Vulcan	Sulphur	British Dyestuffs Corporation.
Wakefield	Acid	F. à Brassard & Co.
Wool	Acid	Various.
Xylene	Acid	Sandoz Chemical Co.
Zambesi	Developed	Berlin Aniline Co.

INDEX TO TABLES.

(The Roman numerals refer to the number of the table, the arabic figures to the division.)

INDEX TO TEXT.

(The figures refer to the pages.)

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